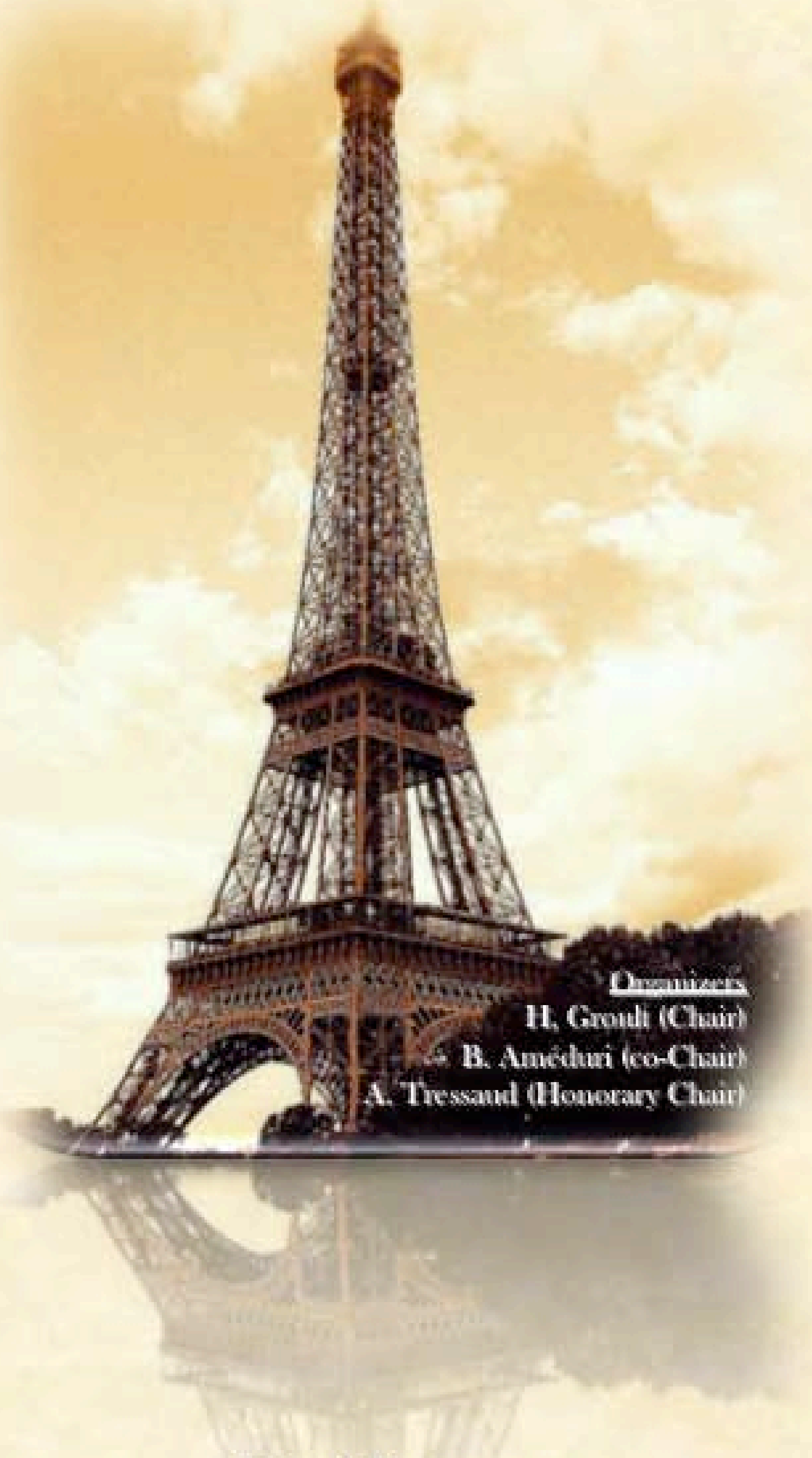
17th ESFC – Paris 2013

# 17th European Symposium on Fluorine Chemistry

Paris, July 21-25, 2013



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Final Program

# Book of Abstracts

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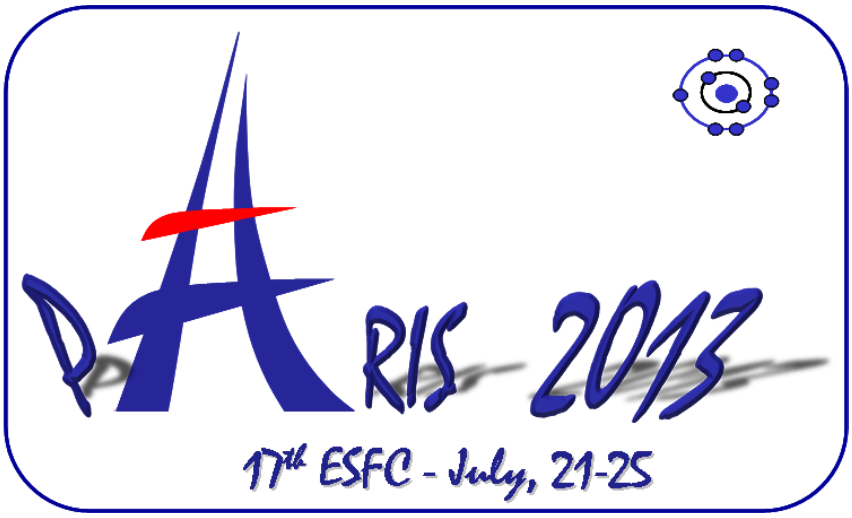
# 17th European Symposium on Fluorine Chemistry



July 21-25, 2013
Paris - France

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# INTRODUCTION

It is a great honor for us to welcome you here in Paris for the 17th European Symposium on Fluorine Chemistry (17th ESFC) which was under the aegis of the *French National Network on Fluorine Chemistry – CNRS* (hppt://www.reseau-fluor.fr).

This symposium held at *Faculté de Pharmacie* (Université Paris Descartes), in the real center of Paris "*Quartier Latin*" (VIth district of Paris) just near the Luxembourg Gardens. For our fluorine chemistry community, this place is a very special and historical landmark since in 1886, Henri Moissan isolated fluorine in one of laboratories of the faculty. To celebrate his memory, an exhibition on Henri Moissan, his life and works, will be displayed at Faculty of Pharmacy from Sunday July 21 afternoon to Monday July 22 evening , and then will move to "Maison de la Chimie" on Tuesday July 22.

From a scientific point of view, the 17th EFSC is addressing to all topics of fluorine chemistry (Organic, Inorganic, Polymer, Biochemistry, Medicine and Material Sciences). It also covers several industrial aspects and the importance of fluorinated products in our daily life. For this event, researchers are coming from all over the world and more than 400 participants from 24 countries are attending this symposium, giving rise to 123 oral communications and 173 posters. Two special events occurring during the sessions must be highlighted:

> i) the first one concerns the Henri Moissan session at "*Maison de la Chimie*" on Tuesday afternoon. During this session, four last laureates of the Henri Moissan Prize will be invited to present a lecture and Bernard Bigot, President of the Foundation of "*Maison de la Chimie*" will introduce the laureate of the 2012 Prize;
>
> ii) the second one, focused on "*Fluorinated Materials for Energy conversion (FMEC II)*", will take place within the scientific sessions and will allow mixing all branches of Fluorine Chemistry involved in such topics: : molten salts, nuclear energy, Li-ion batteries, capacitors, polymer-based fuel cells, etc.

This year coincides also with the 75th anniversary of the discovery of polytetrafluoroethylene (named Teflon® by DuPont) by the chemist Roy Plunkett in DuPont Laboratories, Wilmington, DE (USA). For this reason, and to encourage young talents to work on fluorine chemistry, DuPont has decided to sponsor an award that will be presented to a researcher during the Moissan session. In addition, an "Award of Best Poster on Sustainability" sponsored by Solvay Specialty Polymers will be presented during the cocktail in Paris Vth district - City Hall on Wednesday 24 evening.

More generally, we want to warmly thank all the sponsors that contribute to the success of this symposium.

During your stay, we do hope that you will able to appreciate Paris city and the French way of life through several events: the Cheese & Wine Party during the first poster session, the Banquet taken at "*Maison de la Chimie*", the cruise on Seine river followed by a cocktail in Paris Vth district - City Hall, or the social program that will allow a one day trip to Giverny to visit the Monet's Gardens, or to Versailles for a visit of the Palace … You will have also the opportunity to visit the « *Musée Curie* », very close to the place of the conference, with the memories of four Nobel Prize winners of the same family: Marie Curie- Skłodowska, Pierre Curie, Iréne et Frédéric Joliot-Curie.

Finally, we express our gratitude to the members of the International Advisory Board and of the local organizing committee for their active contribution during the preparation of the scientific program.

We wish you a delicious time in Paris, full of discoveries, fruitful discussions during the conference and we thank you again very much for attending the 17th ESFC.

Paris, July 22, 2013

| | | |
|---|---|---|
| **Henri Groult** | **Bruno Améduri** | **Alain Tressaud** |
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**http://www.17-esfc-paris2013.fr**

# Summary Program

| **Monday, July 22** | | | |
|---|---|---|---|
| | **STREAM A** | **STREAM B** | **STREAM C** |
| 9:00 | Opening Ceremony | | |
| 10:15 | *Coffee* | | |
| **Chair** | **H. Roesky** | | |
| 10:45 | S. L. Buchwald | | |
| 11:30 | R. Hagiwara | | |
| 12:15 | *Lunch* | | |
| Exhibition on Henri Moissan July 21 & 22 | | | |
| **Chair** | **T. Taguchi** | **O. Boltalina** | **M.Pabon** |
| 14:30 | V. Gouverneur | K. Poeppelmeier | P. Metrangolo |
| 15:00 | S. Decamps | C. Pepin | M.P. Krafft |
| 15:20 | M. Rack | I. Flerov | M. Sansotera |
| 15:40 | J. Jaunzems | G. Resnati | P. Kirsch |
| 16:00 | S. Pazenok | C. Legein | C. Murphy |
| 16:30 | *Coffee* | | |
| 17:00 | **Poster session 1 (P1) – Cheeses & Wines Party (from 18:30)** | | |
| **Tuesday, July 23** | | | |
| | **STREAM A** | **STREAM B** | **STREAM C** |
| **Chair** | **B. Crousse** | **R. Hagiwara** | **M.P. Krafft** |
| 9:00 | A. Togni | M. Tramsek | A. Takahara |
| 9:30 | H. Amii | M. Ahrens | M. Wolfs |
| 9:50 | Q. Shen | T. Skapin | H. Hori |
| 10:10 | N. Ignatiev | E. Kanaki | J. Blin |
| 10:30 | *Coffee* | | |
| **Chair** | **T. Yamazaki** | **T. Skapin** | **D. DesMarteau** |
| 11:00 | V. Kukhar | Y.S. Lee | R. Dams |
| 11:30 | S. Ye | T. Goto | P. Crouse |
| 11:50 | L. Hunter | O. Gorban | I. Wlassics |
| 12:10 | A. Tkachenko | F. Simko | T. Irita |
| 12:30 | J. Pytkowicz | S. Ivlev | J. Peyroux |
| 12:50 | *Lunch* | | |
| 15:00 | **Moissan Session at « Maison de la Chimie »** | | |
| 16:00 | **1)** Moissan Prize Awardees *(25min each)*<br>**IL-M1 - Chemical Synthesis of Elemental Fluorine,** by K. O. Christe<br>**IL-M2 - My Favorite Molecules,** by D. DesMarteau<br>**IL-M3- The importance of fluorine in catalysis with organometallic fluorides and in compounds with low valent main group elements,** by H. Roesky<br>**IL-M4- Synthesis and physical chemical properties of inorganic fluorides: "From single crystals to functionalized nanofluorides,** by A. Tressaud<br>**2)** 2012 Moissan Prize<br>**3)** Preview of a movie on Henri Moissan (J. Trouchaud & D. Bour)<br>**4)** DuPont Award - 75th Anniversary of the discovery of Teflon® | | |
| 18:00 | **Cocktail & Banquet** | | |

# Wednesday, July 24

| | STREAM A | STREAM B | STREAM C |
|---|---|---|---|
| **Chair** | **V. Gouverneur** | **E. Antipov** | **I. Wlassics** |
| 9:00 | A. Luxen | O. Boltalina | C.M. Friesen |
| 9:30 | D. O'Hagan | K. Matsumoto | R.W. Read |
| 9:50 | C. Perrio | V. Mitkin | A. Vallribera |
| 10:10 | J. Colomb | D. Lentz | P. Diter |
| 10:30 | *Coffee* | | |
| | **STREAM A** | **STREAM B** | **STREAM FMEC** |
| **Chair** | **Y. Yagupolskii** | **M. Leblanc** | **T. Goto** |
| 11:00 | J.-C. Xiao | P. Lightfoot | R. Konings |
| 11:30 | F. Larnaud | K. Pedersen | S. Delpech |
| 11:50 | T. Hanamoto | W. Grochala | S. Chatain |
| 12:10 | G. Haufe | V. Kharchenko | S. Kuznetsov |
| 12:30 | *Lunch* | | |
| 13:30-15:30 | **Poster Session 2 (P2) - coffee available** | | |
| 16:15-18:30 | **Cruise on Seine river** | | |
| 19:00 | **Reception at Paris Vth district - City Hall”**<br>**Best Poster on Sustainability (Solvay Specialty Polymers)** | | |

# Thursday, July 25

| | STREAM A | STREAM B | STREAM FMEC |
|---|---|---|---|
| **Chair** | **E. Magnier** | **W. Grochala.** | **K. Amine** |
| 9:00 | Y. Yagupolskii | M. Mortier | J.M. Tarascon |
| 9:30 | P. Ivashkin | P. Fedorov | A. Basa |
| 9:50 | K. Shibatomi | Y. Takahira | P. Bonnet |
| 10:10 | M. Medebielle | S. Kuznetsov | D. Meshri |
| 10:30 | *Coffee* | | |
| **Chair** | **H. Koroniak** | **M. Gerken** | **J.-M.Tarascon** |
| 11:00 | T. Yamazaki | G. Schrobilgen | M. Fichtner |
| 11:30 | F. Grellepois | S. Strauss | A. Tasaka |
| 11:50 | V. Sukach | D. Heinrich | D. Dambournet |
| 12:10 | N. Shibata | K. Radan | E. Antipov |
| 12:30 | *Lunch* | | |
| **Chair** | **F. Grellepois** | **S. Brunet** | **T. Nakajima** |
| 14:00 | C. Del Pozo | M. Nappa | J. Thrasher |
| 14:30 | X. Zhan | R. Singh | L. Assumma |
| 14:50 | F. L. Qing | A. Astruc | B. Campagne |
| 15:10 | Y. Budnikova | R. Syvret | C. Bas |
| 15:30 | *Coffee* | | |
| **Chair** | **N. Shibata** | **K. Christe** | **J. Thrasher** |
| 15:50 | S. Thibaudeau | R. Mews | P. Bonnet |
| 16:20 | P.A. Champagne | M. Gerken | T. Nakajima |
| 16:40 | J. Kvicala | K. Seppelt | G. Roeschenthaler |
| 17:00 | A.V. Matsnev | J. Klösener | R. Bouchet |
| 17:20 | H. Yanai | A. Kornath | K. Amine |
| 17:40 | **Conclusions & Farewell Party** | | |

# Conferences

## PLENARY LECTURES

| | | |
|---|---|---|
| **PL1** | **S. L. BUCHWALD** | Palladium-catalyzed methods for the synthesis of fluorinated compounds: progress and mechanistic studies |
| **PL2** | **R. HAGIWARA** | Ionic liquid and mesophase fluorides for electrolyte applications |

## INVITED LECTURES

| | | |
|---|---|---|
| **IL-A1** | **V. GOUVERNEUR** | Catalytic fluorination and trifluoromethylation |
| **IL-A2** | **S. PAZENOK** | Fluorocontaining pyrazoles – versatile building blocks for agrochemicals |
| **IL-B1** | **K. POEPPELMEIER** | Synthesis of noncentrosymmetric oxide-fluorides |
| **IL-B2** | **C. LEGEIN** | Assignment of $^{19}$F NMR resonances and prediction of $^{19}$F isotropic chemical shifts of inorganic fluorides: $\alpha$-LaZr$_2$F$_{11}$, NbF$_5$ and TaF$_5$ |
| **IL-C1** | **P. METRANGOLO** | Supramolecular chemistry with perfluoroalkyl iodides |
| **IL-C2** | **C. MURPHY** | Biofilm-catalysed transformation of organofluorine compounds |
| **IL-A3** | **A. TOGNI** | Heteroatom trifluoromethylation |
| **IL-B3** | **M. TRAMŠEK** | XeF$_2$: interesting ligand in coordination compounds and useful oxidizing agent |
| **IL-C3** | **A. TAKAHARA** | Surface structure and wetting behavior of fluoroacrylate polymers |
| **IL-A4** | **V. KUKHAR** | Fluorine-containing amino phosphonates. a family of bioactive molecules |
| **IL-B4** | **Y. S. LEE** | Carbon nano-materials for electric double layer capacitance |
| **IL-C4** | **R. DAMS** | Fluoropolyether elastomers having low glass transition temperatures |
| **IL-A5** | **A. LUXEN** | Applications of PET in medical imaging |
| **IL-B5** | **O. BOLTALINA** | Fluorocarbon organic acceptors: fundamentals and applications |
| **IL-C5** | **C. M. FRIESEN** | Innovative methodology for the preparation of quaternary ammonium perfluoroalkoxides |

| | | |
|---|---|---|
| **IL-A6** | **J.-C. Xiao** | Synthesis & reaction of some fluorine-containing phosphonium salts |
| **IL-B6** | **P. Lightfoot** | Magnetic frustration in vanadium fluoride-based kagome lattices |
| **IL-FMEC6** | **R. Konings** | The chemistry of molten salt reactor fuel |
| **IL-A7** | **Y. Yagupolskii** | A novel non catalytic C-H perfluoroalkylation of aromatic substrates by $RfSiMe_3$ based on activation of π-system |
| **IL-B7** | **M. Mortier** | Rare earth doped inorganic fluoride materials: synthesis and applications |
| **IL-FMEC7** | **J. M. Tarascon** | F-based materials for Li-ion batteries |
| **IL-A8** | **T. Yamazaki** | Convenient stereoselective synthesis of β-Perfluoroalkyl-β-alkyl α,β-Unsaturated Esters |
| **IL-B8** | **G.J. Schrobilgen** | New developments in synthetic and structural noble-gas chemistry; The Coordination Behaviors of $NgF_2$ (Ng = Kr, Xe) Towards Metal and Non-Metal Centers; and the Syntheses of $FXeOXO_3$ (X = Cl, Br) and Related $XO_2^+$ Complexes of $NgF_2$ |
| **IL-FMEC8** | **M. Fichtner** | Batteries based on metal halides |
| **IL-FMEC9** | **E. Antipov** | New fluorine-containing cathode materials for Li-ion batteries |
| **IL-A9** | **C. Del Pozo** | New transformations of fluorinated alkynes mediated by transition metals |
| **IL-B9** | **M. Nappa** | Recent advances in developing new low GWP alternatives to HFC & HCFC |
| **IL-FMEC10** | **J.S. Thrasher** | Novel low EW, water insoluble perfluoro-sulfonimide (PFSI) ionomers |
| **IL-A10** | **S. Thibaudeau** | Fluorination in superacid $HF/SbF_5$ |
| **IL-B10** | **R. Mews** | Triple bond systems of sulfur |
| **IL-FMEC11** | **P. Bonnet** | Arkema's advances in fluorochemical technologies for lithium ion battery |
| **IL-FMEC12** | **K. Amine** | Advanced next generation high energy lithium battery |
| **IL-M1** | **K. O. Christe** | Chemical synthesis of elemental fluorine |
| **IL-M2** | **D. DesMarteau** | My favourite molecules |
| **IL-M3** | **H. Roesky** | The importance of fluorine in catalysis with organometallic fluorides and in compounds with low valent main group elements, |
| **IL-M4** | **A. Tressaud** | Synthesis and physical chemical properties of inorganic fluorides: "From single crystals to functionalized nanofluorides, |

# MONDAY, JULY 22

# Monday, July 22

**9:00 – 10:15** **OPENING CEREMONY**

**10:15 – 10:45** *Coffee break*

**An Exhibition on Henri Moissan, his life and his works, will be displayed at *Faculty of Pharmacy* from Sunday July 21 afternoon to Monday July 22 evening**

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**<u>CHAIR</u>: H. ROESKY, *University of Göttingen (Germany)***

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**Plenary lectures**

**10:45 PL1** **PALLADIUM-CATALYZED METHODS FOR THE SYNTHESIS OF FLUORINATED COMPOUNDS: PROGRESS AND MECHANISTIC STUDIES**

**S. L. Buchwald,**

*MIT, Dept. of Chemistry, Cambridge, MA (USA)*

**11:30 PL2** **IONIC LIQUID AND MESOPHASE FLUORIDES FOR ELECTROLYTE APPLICATIONS**
**R. Hagiwara,**
*Kyoto University, Graduate School of Energy Science, Kyoto (Japan)*

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**12:15 – 14:00** *Lunch*

## STREAM A

**<u>CHAIR</u>: T. TAGUCHI, *Sagami Chemical Research Institute (Japan)***

**14:30 IL-A1** **<u>Invited Lecture</u>**
**CATALYTIC FLUORINATION AND TRIFLUOROMETHYLATION**
**V. Gouverneur,**
*Oxford University, Chemistry Research Laboratory (UK)*

**15:00 A1.1** **FLUORINATED INHIBITORS OF CARBAPENEMASES: FIGHTING ANTIBIOTIC-RESISTANT GRAM-NEGATIVE BACTERIA**
**S. Decamps,** B. Crousse, S. Ongeri
*Université Paris-Sud, BIOCIS, Châtenay-Malabry (France)*

**15:20 A1.2** **THE VALUE OF FLUORINE IN AGRICULTURAL CHEMISTRY**
**M. Rack**, M. Budich, S. Smidt, P. Schäfer, G. Hamprecht, J. Gebhardt, H. Isak, J. Rheinheimer, C. Koradin, V. Maywald, T. Zierke, B. Wolf
*BASF SE, Global Research and Development Crop Protection, Ludwigshafen (Germany)*

**15:40** **A1.3** **A GREEN ROUTE TO ETHYL 3-(DIFLUOROMETHYL)-1-METHYL-1H-PYRAZOLE-4-CARBOXYLATE (DFMMP)**
**J. Jaunzems**, M. Braun
*Solvay Fluor GMbH, R&D Fluoro Organic Specialities, Hannover (Germany)*

**16:00** **IL-A2** **Invited Lecture**
**FLUOROCONTAINING PYRAZOLES - VERSATILE BUILDING BLOCKS FOR AGROCHEMICALS**
**S. Pazenok**
*Bayer CropScience, BCS AG-R&D-SMR-RT, Monheim (Germany)*

## STREAM B

CHAIR: **O. BOLTALINA, *Colorado State University* (USA)**

**14:30** **IL-B1** **Invited Lecture**
**SYNTHESIS OF NONCENTROSYMMETRIC OXIDE-FLUORIDES**
**K. Poeppelmeier**
*Northwestern University, Chemistry Dept, Evanston, IL (USA)*

**15:00** **B1.1** **$Co^{3+}$-BASED FLUORIDES USED AS FLUORINATING AGENTS**
**C. Pepin**, A. Demourgues, E. Durand, A. Tressaud
*ICMCB-CNRS, Pessac (France)*

**15:20** **B1.2** **STRUCTURE, PHYSICAL PROPERTIES AND PHASE TRANSITIONS IN $(NH_4)_2TiF_6{\cdot}NH_4F$**
**I. Flerov**, E. Pogoreltsev, S. Mel'nikova, M. Gorev, A. Kartashev, E. Bogdanov, M. Molokeev, N. Laptash
*Kirensky Institute of Physics, Crystalphysics Lab, Krasnoyarsk (Russia)*

**15:40** **B1.3** **FLUORINATED METAL-ORGANIC FRAMEWORKS FORMED UNDER HALOGEN BOND CONTROL**
**G. Resnati**, L. Colombo, G. Cavallo, P. Metrangolo, G. Terraneo
*Politecnico di Milano, Dept of Chemistry, NFMLAB (Italy)*

**16:00** **IL-B2** **Invited Lecture**
**ASSIGNMENT OF $^{19}F$ NMR RESONANCES AND PREDICTION OF $^{19}F$ ISOTROPIC CHEMICAL SHIFTS OF INORGANIC FLUORIDES: $\alpha$-$LaZr_2F_{11}$, $NbF_5$ AND $TaF_5$**
**C. Legein,** M. Biswal, M. Body, F. Fayon, F. Boucher, C. Martineau, A. Sadol
*Université du Mans, IMMM, CNRS UMR 6283 (France)*

# STREAM C

CHAIR: **M. PABON, *DuPont de Nemours (Switzer land)***

| | | |
|---|---|---|
| **14:30** | **IL-C1** | Invited Lecture<br>**SUPRAMOLECULAR CHEMISTRY WITH PERFLUOROALKYL IODIDES**<br>G. Cavallo, **P. Metrangolo**, G. Resnati, G. Terraneo<br>*Politecnico di Milano, NFMLAB - Dept of Chemistry, Materials & Chemical Engineering (Italy)* |
| **15:00** | **C1.1** | **COMPETITIVE ADSORPTION OF PHOSPHOLIPIDS AND PROTEINS AT AN AIR/WATER INTERFACE: A FLUOROCARBON GAS CAN BOOST ITS KINETICS**<br>P. N. Nguyen, G. Waton, T. Vandamme, **M. P. Krafft**<br>*Université de Strasbourg, Institut Charles Sadron-CNRS (France)* |
| **15:20** | **C1.2** | **CHEMICAL LINKAGE OF PERFLUOROPOLYETHER CHAINS TO CARBON-BASED NANOMATERIALS: RECENT RESULTS AND NEW PERSPECTIVES**<br>**M. Sansotera**, S. Talaeemashhadi, M. Gola, C. Bianchi, P.A. Guarda, W. Navarrini<br>*Politecnico di Milano, Dept of Chemistry (Italy)* |
| **15:40** | **C1.3** | **EXPLORING CONFORMATIONAL SPACE: STEREOELECTRONIC EFFECTS FOR THE DESIGN OF NEMATIC LIQUID CRYSTALS**<br>**P. Kirsch,**<br>*Merck KGaA, Liquid Crystal R&D Chemistry, Darmstadt (Germany)* |
| **16:00** | **IL-C2** | Invited Lecture<br>**BIOFILM-CATALYSED TRANSFORMATION OF ORGANOFLUORINE COMPOUNDS**<br>**C. Murphy**<br>*University College Dublin, Biomolecular & Biomedical Science (Ireland)* |
| **16:30 – 17:00** | | *Coffee* |
| **17:00 - 20:00** | | **POSTER SESSION 1 + CHEESE PARTY (FROM 18:30)** |

# PLENARY LECTURES

## MONDAY, JULY 22

**PL1**

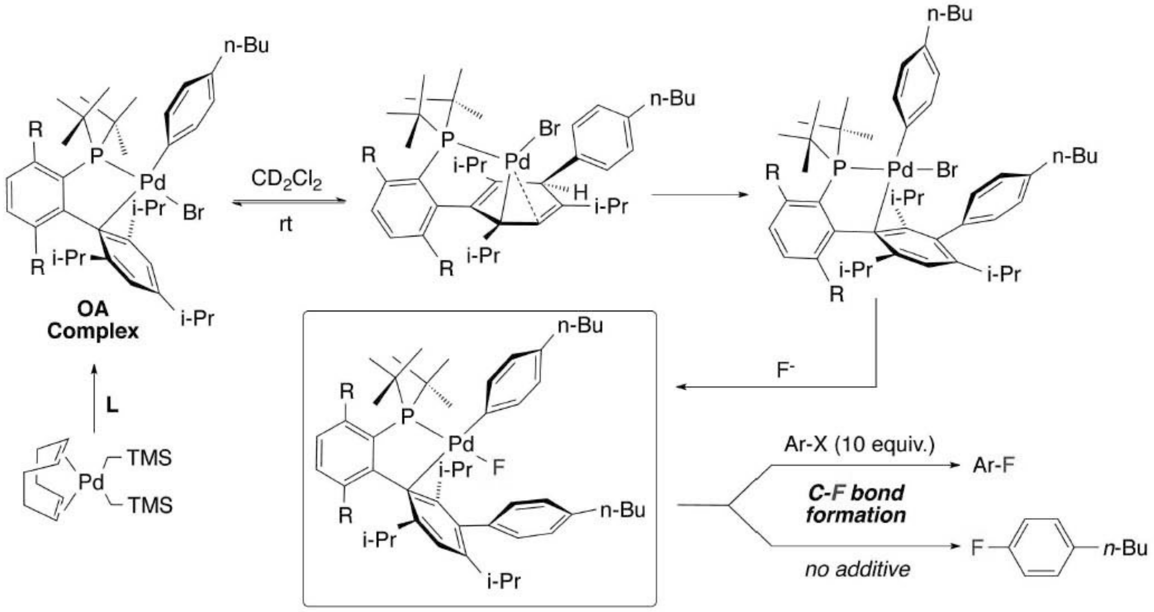
# Palladium-Catalyzed Methods for the Synthesisof Fluorinated Compounds: Progress and Mechanistic Studies

**S.L. BUCHWALD** [(a)]*

(a) MIT, Dpt. of Chemistry - CAMBRIDGE (UNITED STATES)

* sbuchwal@mit.edu

We have recently reported on the use of palladium catalysts for the conversion of aryl triflates to aryl fluorides. Since our original paper, we have uncovered a variety of mechanistic features of this process, many of which are unprecedented. Using this knowledge, we have been able to arrive at improved catalysts as well as to increase the user friendliness of the process. An overview of these and our latest results will be presented.



## PL2

# Ionic liquid and mesophase fluorides for electrolyte applications

**R. HAGIWARA** [(a)]*

[(a)] KYOTO UNIVERSITY, GRADUATE SCHOOL OF ENERGY SCIENCE - KYOTO (JAPAN)

* hagiwara@energy.kyoto-u.ac.jp

Liquid onium fluorohydrogenates, $Cat^+(FH)_nF^-$, are non-volatile and non-flammable, relatively low viscous among room temperature ionic liquids. Some of them exhibit high ionic conductivities exceeding 100 mS $cm^{-1}$ at ambient temperature. The highest ionic conductivity among RTILs, 131 mS $cm^{-1}$, has been recorded recently for a trimethylsulfonium salt [1]. Application of these fluorohydrogenate ILs will be introduced for the electrolytes of electrochemical capacitors [2] and fuel cells operating at middle-ranged temperatures [3].

*N*,*N*-dimethylpyrrolidinium fluorohydrogenate ($DMPyr(FH)_2F$) and *N*-ethyl-*N*-methylpyrrolidinium fluorohydrogenate ($EMPyr(FH)_2F$) give ionic plastic crystal phases of rock salt type structure around room temperature, respectively [4]. Ionic conductivities range from $10^0$ to $10^1$ mS $cm^{-1}$. Tetraethylphosphonium fluorohydrogenate salt, $P_{2222}(FH)_2F$, exhibits two plastic crystal phases [5]. The high temperature phase has a hexagonal lattice which is the first example of a plastic crystal with an inverse nickel arsenide-type structure, exhibiting a conductivity of 5 mS $cm^{-1}$ at 323 K. Liquid crystalline mesophases with a smectic A interdigitated bilayer structure are observed for 1-alkyl-3-methylimidazolium fluorohydrogenate salts, $C_x MIm(FH)_2F$ ($x$ = 10, 12, 14, 16, and 18) [6]. The liquid crystalline mesophase of $C_{12}MIm(FH)_2F$ exhibits anisotropy in ionic conductivity and the conductivity parallel to the smectic layer is roughly ten times larger than that perpendicular to it.

We have recently developed an eutectic molten amide mixture, NaFSA-KFSA (FSA=bis(fluorosulfonyl)amide) as a promising electrolyte for sodium rechargeable batteries operating at intermediate temperatures (60-120°C) [7]. The cell performances will be discussed on the batteries using FSA-based ionic liquid electrolytes.

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# STREAM A

## MONDAY, JULY 22

## IL-A1

# Catalytic Fluorination and Trifluoromethylation

**V. GOUVERNEUR** (a)*

(a) UNIVERSITY OF OXFORD, CHEMISTRY RESEARCH LABORATORY - OXFORD (UK)

* veronique.gouverneur@chem.ox.ac.uk

Fluorine has become a powerful foundation for chemical exploration, discovery and innovation. We are interested in all aspects of selective fluorination with the design, discovery, and study of fundamentally interesting and useful organic reactions. The control of absolute and relative stereochemistry in C-F bond construction is an underlying goal in much of this work because of the crucial role played by the three-dimensional structure of molecules in their function. Our current efforts towards the design and implementation of transition-metal based strategies to activate or construct C-F/C-$CF_3$ bond will be discussed. The value of the chemistry will be exemplified in the context of $^{18}$F-radiochemistry to support positron emission tomography, a molecular imaging technology of clinical value for diagnosis, personalized medicine and drug development.

## A1.1

# Fluorinated inhibitors of carbapenemases: Fighting antibiotic-resistant gram-negative bacteria

**S. DECAMPS** [(a)]*, **B. CROUSSE** [(b)], **S. ONGERI** [(c)]

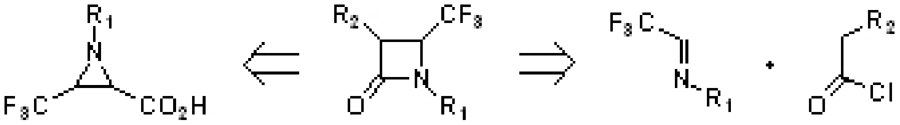
[(a)] UNIVERSITÉ PARIS-SUD, BIOCIS - CHATENAY-MALABRY (FRANCE)
[(b)] Faculté de Pharmacie Université Paris Sud, BIOCIS MOLECULES FLUORÉES ET CHIMIE MÉDICINALE CHÂTENAY-MALABRY (FRANCE)
[(c)] UNIVERSITÉ PARIS SUD, MOLÉCULES FLUORÉES ET CHIMIE MÉDICINALE, UMR CNRS 8076, LABEX LERMIT CHÂTENAY-MALABRY (FRANCE)

* sophie.decamps@u-psud.fr

Multidrug resistant (MDR) gram-negative pathogens, especially *Enterobacteriaceae*, are emerging worldwide. This is particularly worrisome in view of the actual dearth of new compounds active against MDR gram-negative bacteria in the pipeline. Currently, utility of widely prescribed β-lactam antibiotics is being threatened by the proliferation of strains producing β-lactamases (BL), enzymes with broad hydrolytic abilities. Combining the use of β-lactams with BL inhibitors has proved a valuable strategy to overcome resistances. However, the lack of inhibitors active against strains producing carbapenemases (challenging activity of even the newest β-lactams, carbapenems) is a matter of concern[1].

As part of continuing efforts to discover new carbapenemase inhibitors, we are interested in design and synthesis in new trifluoromethylated monobactams. Indeed, it is suggested in the literature that introducing an electron-withdrawing fluorinated substituent on the β-lactam ring would have a good effect on antibacterial activity. Moreover, thanks to their characteristic lipophilicity and strength of CF bond, fluoroalkyl groups confer interesting properties to biologically active molecules.

While diverse methods are well known to access β-lactams ring, few publication describe the formation of β-lactams trifluoromethylated in C-4 position[2][3]. Based on previously obtained results in our laboratory[2], we herein report the synthesis of new trifluoromethylated monobactams through Staudinger reaction and ring enlargement of aziridines[4]. These new compounds will be further tested as potential carbapenemase inhibitors.



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## A1.2

# The Value of Fluorine in Agricultural Chemistry

**M. RACK** [(a)]*, **M. BUDICH** [(a)], **S. SMIDT** [(a)], **P. SCHÄFER** [(a)], **G. HAMPRECHT** [(a)], **J. GEBHARDT** [(a)], **H. ISAK** [(a)], **J. RHEINHEIMER** [(a)], **C. KORADIN** [(a)], **V. MAYWALD** [(a)], **T. ZIERKE** [(a)], **B. WOLF** [(a)]

[(a)] BASF SE, GLOBAL RESEARCH AND DEVELOPMENT CROP PROTECTION, GVA/PD - LUDWIGSHAFEN (GERMANY)

* michael.rack@basf.com

Inventing, developing, and commercializing new chemistry and products rapidly is a key for sustained profitability in the agrochemical, fine and specialty chemical, and pharmaceutical markets. New products will require the development of efficient synthetic routes and robust manufacturing processes. The presentation will give an overview of the latest fluorinated agrochemical active ingredients developed at the BASF crop protection division during the last years. Methods for their synthesis, an insight into the route scouting efforts, process development and different ways for the synthesis of certain key fluorine containing intermediates will be presented.

## A1.3

# A Green Route to Ethyl 3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxylate (DFMMP)

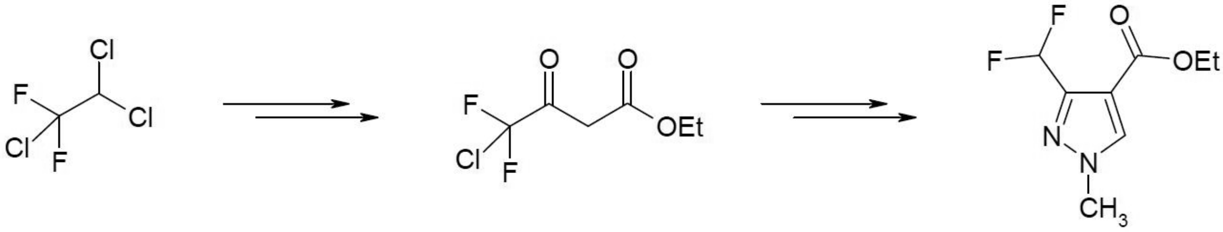
**J. JAUNZEMS [(a)]*, M. BRAUN [(a)]**

[(a)] Solvay Fluor GmbH, R&D FLUORO ORGANIC SPECIALITIES - HANNOVER (GERMANY)

* janis.jaunzems@solvay.com

Growing number of fluorine containing active ingredients in pharmaceutical and agrochemical industry inevitably raises demand of new fluorinated building blocks. Their availability is mainly constricted by suitable chemistry and available bulk fluorine containing starting materials. Due to high cost impact especially in agrochemical industry, the choice of synthesis route is heavily driven by economical aspects, thus environmental profile is often handled as „secondary factor" or  finally fall aside.

DFMMP is a key building block for a fast growing new fungicide family, like Syngenta's Sedaxane®, and BASF's Fluxapyroxad® and Bayer´s Bixafen® currently made by a environmetally less friendly route. Herein, we present a cost competitive and green route, developed at Solvay labs displaying significantly lower environmental impact.



## IL-A2

# Fluorocontaining pyrazoles – versatile building blocks for agrochemicals

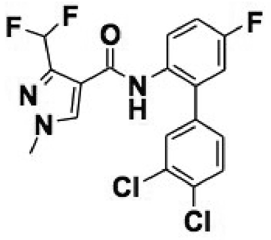
**S. PAZENOK** [(a)*]

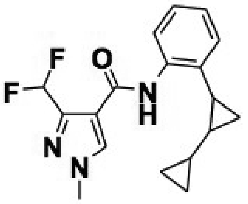
[(a)] Bayer CropScience, Process Research - MONHEIM (GERMANY)

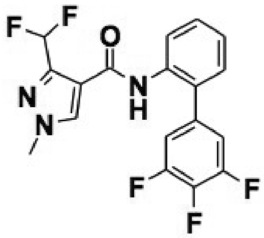
* sergiy.pazenok@bayer.com

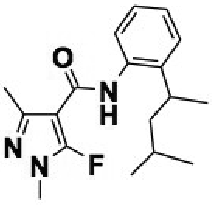
The introduction of fluorine atoms into lead structures is powerful strategy to optimize the properties of agricultural and pharmaceutical products.[1] Hence, a significant rise in the number of active ingredients containing at least one fluorine atom has been observed over the last decades, and a recent survey estimated that as many as 18% of the pesticides on the market were fluorinated compounds.[2] Among the vast array of fluorine-containing functionalities fluoroalkyl pyrazoles have attracted considerable attention due to their potential enhanced biological properties [3]. In particular, a huge interest was accorded to the difluoromethyl pyrazole-carboxamides and 3-methyl-5-fluoro pyrazole-carboxamides which belong to the class of succinate-dehydrogenase inhibitors (SDHI) fungicides (Figure 1). Several different compounds of this class were recently introduced to the crop protection market.

Different synthetic approaches to the diversely Fluorinated Pyrazoles will be presented and discussed.









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# STREAM B

MONDAY, JULY 22

## IL-B1

# Synthesis of Noncentrosymmetric Oxide-fluorides

**K. POEPPELMEIER** [(a)]*

[(a)] NORTHWESTERN UNIVERSITY, CHEMISTRY DEPARTMENT - EVANSTON IL (USA)

* krp@northwestern.edu

This talk will discuss the use of oxide-fluoride chemistry to create new frequency doubling materials and their potentially-improved efficiencies and absorptions. Noncentrosymmetric oxide-fluoride materials are desired for use as frequency doublers (FDs): crystals that are able to double the frequency of laser light to obtain higher energy laser sources. Fluoride ions within solid-state early-transition metal oxides can enhance the efficiency of the FD response and blue shift the absorption of the material so that the material does not absorb laser light in the FD process. Absorption of the laser light can both damage the crystal and decrease the FD. Typically, noncentrosymmetric compounds are synthesized with polar units (such as early-transition metals). We examined the distorted anion of $[VOF_4(H_2O)]^{2-}$ within the series of compounds $MVOF_4(H_2O)_7$ ($M^{2+}$ = Co, Ni, Cu, Zn). $CuVOF_4(H_2O)_7$ was the only compound to crystallize in a noncentrosymmetric space group owing to the packing of bent units and exhibit FD behavior. It is also possible to synthesize polar materials from racemates. One such material is $[Cu(H_2O)(bpy)_2]_2[HfF_6]_2\cdot 3H_2O$ that has Λ- and Δ-$[Cu(H_2O)(bpy)_2]_{2+}$ cations arranged so that only mirror or glide planes relate the two enantiomers which is a condition to observe the polarity.

## B1.1

# $Co^{3+}$-based fluorides used as fluorinating agents

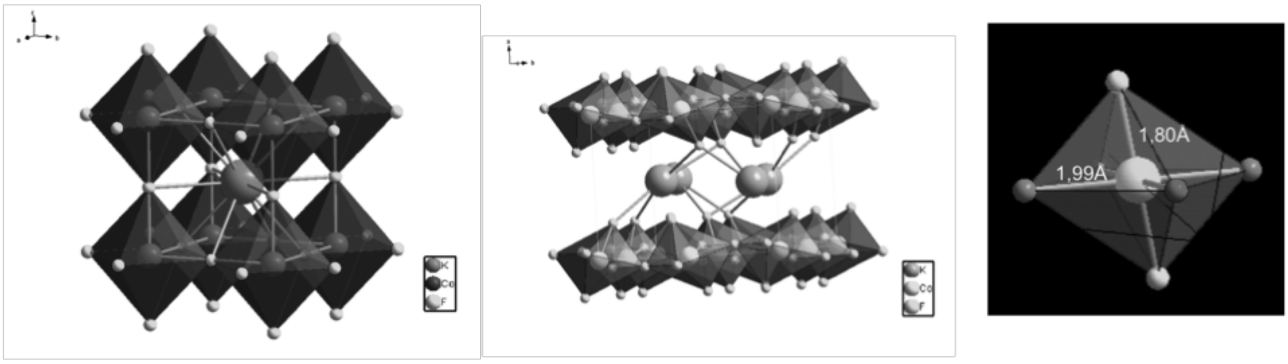
**C. PEPIN** [(a)], **A. DEMOURGUES** [(a)*], **E. DURAND** [(a)], **A. TRESSAUD** [(a)]

[(a)] ICMCB-CNRS, Université Bordeaux 1 - PESSAC (FRANCE)

* demourg@icmcb-bordeaux.cnrs.fr

High valency metal fluorides ($Ce^{IV}$, $Pr^{IV}$, $Tb^{IV}$, $Mn^{IV}$, $Co^{III}$, $Ni^{IV}$, $Ag^{II}$) such as Cobalt trifluoride ($CoF_3$) and Potassium Cobalt tetrafluoride ($KCoF_4$) have been used as fluorinating agent to get fluoro-compounds (1,2). In the last ten years, numerous works have been devoted to the synthesis and characterization of divided inorganic fluorides with High Surface Areas in order to improve their reactivity and catalytic activity (3,4).

Unconventional route such as microwave-assisted solvothermal synthesis(3,4) allow preparing $KCoF_3$ and $CoF_2$ compounds with surface areas equal to $50 m^2/g$ and $30 m^2/g$ respectively. After a $F_2$-direct fluorination at T=200°C (10%$F_2$) the surface area decreases to $8 m^2/g$ for $KCoF_4$ whereas it increases surprisingly to $55 m^2/g$ for $CoF_3$. The $KCoF_3$ perovskite 3D-network (SG: Pm-3m) transforms into perovskite layers 2D-structure $KCoF_4$ (SG: Pbnm) where $Co^{3+}$ ions are stabilized in original flattened octahedral site. Edge and corner-sharing $Co^{2+}$ octahedral sites in rutile-$CoF_2$ become corner-sharing $Co^{3+}$ octahedral sites stabilized in $CoF_3$ derived 3D-perovskite. Thermogravimetric analyses under He of $Co^{3+}$-based fluorides which leads to the loss of one fluorine atom (1/2 $F_2$) at low temperature, reveal various behaviors which strongly depend on the composition, the surface areas and the structural features.



*Crystal structures of $KCoF_3$, $KCoF_4$ and flattened octahedral site of $Co^{3+}$ in $KCoF_4$.*

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## B1.2

# Structure, physical properties and phase transitions in $(NH_4)_2TiF_6{\cdot}NH_4F$

**I. FLEROV** [(a)*], **E. POGORELTSEV** [(b)], **S. MEL'NIKOVA** [(b)], **M. GOREV** [(b)], **A. KARTASHEV** [(b)], **E. BOGDANOV** [(b)], **M. MOLOKEEV** [(b)], **N. LAPTASH** [(c)]

[(a)] Kirensky Institute of Physics, SB RAS, CRYSTALPHYSICS LAB - KRASNOYARSK (RUSSIA)
[(b)] Kirensky Institute of Physics, SB RAS - KRASNOYARSK (RUSSIA)
[(c)] Institute of Chemistry, FEB RAS - VLADIVOSTOK (RUSSIA)

* flerov@iph.krasn.ru

Fluorine compounds $A_2A'MeF_x$, $A_3MeF_x$, $A_2MeF_x$ (A, A′ = K, Rb, Cs, $NH_4$) containing anionic species $[MeF_x]$ (x = 6, 7) are known to crystallize in many different crystal structures depending on the central atom valency. Some of them undergo structural phase transitions and show interesting behaviour of physical properties important from the fundamental and practical points of view [1].

In this paper we present the results of structure, heat capacity, thermal dilatation, twinning, birefringence, permittivity and susceptibility to hydrostatic pressure investigations of fluoride with seven F atoms in the formula unit, $(NH_4)_3TiF_7=(NH_4)_2TiF_6{\cdot}NH_4F$, and with six-coordinated anionic polyhedra $TiF_6^{-2}$. In heating and cooling cycles the physical properties have shown reversible anomalous behaviour at $T_1$ = 360 K and $T_2$ = 295 K. Rather intriguing succession of the first order phase transitions was found in polarizing optic and X-ray powder diffraction measurements: the symmetry of the crystal lattice increases with the temperature decrease – Tetragonal 1 ($T_1$) → Tetragonal 2 ($T_2$) → Cubic (Fig. 1.). At the same time the structural disorder is strongly decreased and significant entropy changes are characteristic for order-disorder phase transitions. According to T-p phase diagram, hydrostatic pressure narrows the interval of intermediate phase existence.

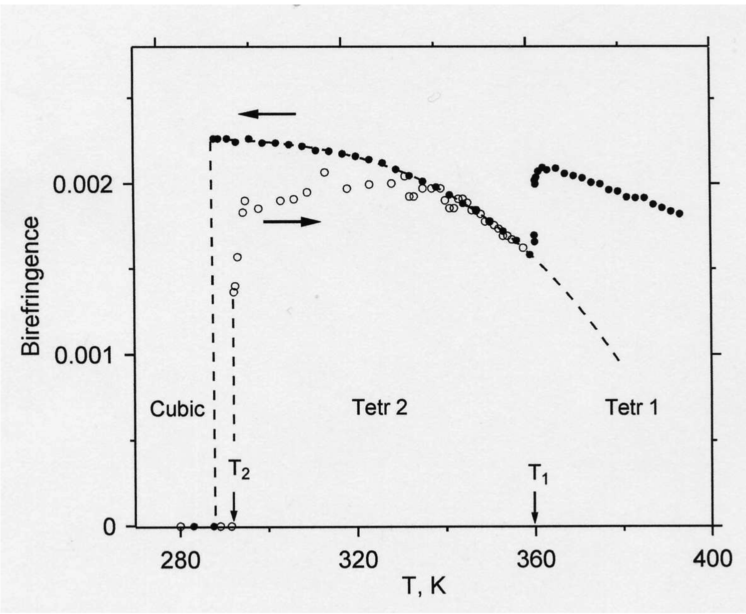

*Fig. 1. Temperature behaviour of the birefringence*

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## B1.3

# Fluorinated Metal-Organic Frameworks Formed under Halogen Bond Control

**G. RESNATI** [(a)]*, **L. COLOMBO** [(a)], **G. CAVALLO** [(a)], **P. METRANGOLO** [(a)], **G. TERRANEO** [(a)]

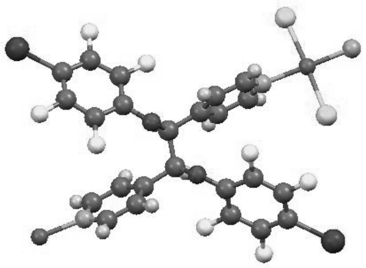
[(a)] NFMLAB-DCMIC “Giulio Natta”, Politecnico di Milano, NFMLAB - DEPT OF CHEMISTRY, MATERIALS AND CHEMICAL ENGINEERING - MILANO (ITALY)

* giuseppe.resnati@polimi.it

The last two decades have seen a growing interest in the field of Metal-Organic Frameworks (MOFs), i.e. crystalline materials composed of self-assembled organic ligands and metal cations. The wide set of available components enables the construction of networks with tuneable properties. Applications are in areas as diverse as gas storage and separation[1] or catalysis[2]. In the last years, the fascinating and useful properties of fluorinated molecules prompted the preparation of MOFs containing fluorinated ligands (F-MOFs). Enhanced thermal and chemical stability, high hydrophobicity of the pores, low surface energy, and low refractive index are expected. Only a few F-MOFs structures have been reported to date, mainly related to gas absorption, especially $H_2$[3]. Other examples of F-MOFs include magnetic materials, near IR emitting networks, and fluorescent frameworks.

Tuning the properties of the network via structural control is one of the main challenges in the MOFs field. Coordination bonds (CBs) are the main driving force in the self-assembly process of MOFs, but other supramolecular interactions such as hydrogen bonds (HBs), halogen bonds (XBs), π-π stacking play a significant role. The strong electron withdrawing effect of fluorine makes perfluorinated molecules containing a different halogen atom particularly tailored to the formation of strong XBs and we decided to pursue the synergy of XB and CB in the self-assembly of F-MOFs.

Here we report a new Cu(II)-F-MOF containing unsaturated metal centres showing selective and reversible solvent absorption accompanied by solvatochromic effect. The framework has been realized employing the new ligand *rac*-4,4'-[1,2-bis(2,3,5,6-tetrafluoro-4-iodophenoxy)ethane-1,2-diyl]dipyridine (1) which has been specifically designed to be involved in XBs, HBs and CBs.[4]



*Minimum unit of the the Cu(II)-F-MOF.*

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## IL-B2

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# Assignment of $^{19}F$ NMR resonances and prediction of $^{19}F$ isotropic chemical shifts of inorganic fluorides: α-$LaZr_2F_{11}$, $NbF_5$ and $TaF_5$.

**C. LEGEIN** [(a)]*, **M. BISWAL** [(a)], **M. BODY** [(a)], **F. FAYON** [(b)], **F. BOUCHER** [(c)], **C. MARTINEAU** [(d)], **A. SADOC** [(c)]

[(a)] IMMM, CNRS UMR 6283, INSTITUT DES MOLÉCULES ET DES MATÉRIAUX DU MANS (IMMM), UMR CNRS 6283 - LE MANS CEDEX 9 (FRANCE)
[(b)] CEMHTI, CNRS UPR 3079 - ORLEANS CEDEX 2 (FRANCE)
[(c)] Institut des Matériaux Jean Rouxel (IMN) - NANTES CEDEX 3 (FRANCE)
[(d)] Tectospin, Institut Lavoisier de Versailles (ILV), CNRS UMR 8180 - VERSAILLES (FRANCE)

* Christophe.Legein@univ-lemans.fr

The efficiency of $^{19}F$ solid state NMR and DFT calculations for the assignment of $^{19}F$ NMR resonances and the prediction of $^{19}F$ isotropic chemical shifts ($\delta_{iso}$) of inorganic fluorides is illustrated on three compounds, α-$LaZr_2F_{11}$ [1], $NbF_5$ and $TaF_5$ [2].

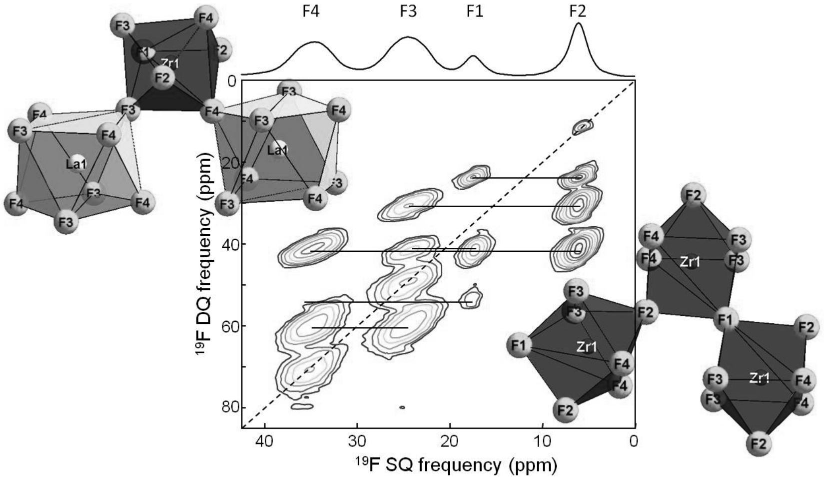

*Fig. 1. $^{19}F$ 2D DQ-SQ MAS (64 kHz) NMR correlation spectrum of α-$LaZr_2F_{11}$ recorded at a magnetic field of 17.6 T. The projection of the 2D spectrum onto the $^{19}F$ SQ dimension is shown on top with resonance assignment.*

The crystal structure of α-$LaZr_2F_{11}$ has been refined from X-ray powder diffraction data. It contains four F inequivalent crystallographic sites. $^{19}F$ 1D MAS NMR spectra of α-$LaZr_2F_{11}$ are in agreement with the proposed structural model. Assignment of the $^{19}F$ resonances to the corresponding crystallographic sites has been performed on the basis of both their relative intensities and their correlation patterns in a $^{19}F$ 2D dipolar-based double-quantum recoupling MAS NMR spectrum (Fig. 1). DFT calculations of the $^{19}F$ chemical shielding tensors have been performed using the GIPAW method, for experimental and optimized structures. A relatively nice agreement is obtained between the experimental $^{19}F$ isotropic and anisotropic chemical shifts and the values calculated for the proposed structural model.

The $^{19}F$ $\delta_{iso}$ values of $NbF_5$ and $TaF_5$, which are isostructural and involve six fluorine sites, have been determined from the reconstruction of 1D $^{19}F$ MAS NMR spectra. The $^{19}F$ chemical shielding tensors have been calculated, using the GIPAW method, for initial and optimized structures. A complete and unambiguous assignment of the $^{19}F$ NMR lines of $NbF_5$ and $TaF_5$ is obtained, ensured by the linearity between experimental $^{19}F$ $\delta_{iso}$ values and calculated $^{19}F$ $\sigma_{iso}$ values. The relationships between the $^{19}F$ $\delta_{iso}$ values, the nature of the fluorine atoms (bridging or terminal), the axial or equatorial position of the terminal ones, the fluorine charges, the ionicity and the length of the M-F bonds have been established.

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# STREAM C

## MONDAY, JULY 22

## IL-C1

# Supramolecular Chemistry With Perfluoroalkyl Iodides

**G. CAVALLO** [(a)], **P. METRANGOLO** [(a)]*, **G. RESNATI** [(a)], **G. TERRANEO** [(a)]

[(a)] NFMLAB-DCMIC “Giulio Natta”, Politecnico di Milano, NFMLAB - DEPT OF CHEMISTRY, MATERIALS AND CHEMICAL ENGINEERING - MILANO (ITALY)

* pierangelo.metrangolo@polimi.it

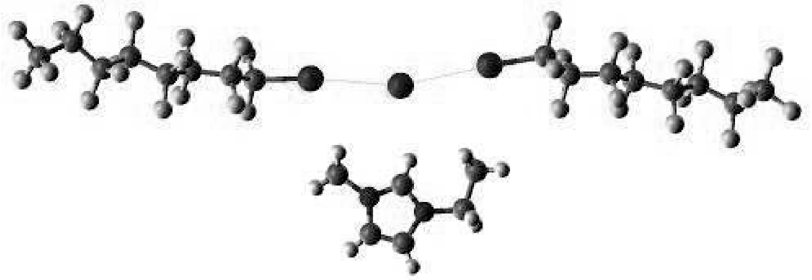

Fig. 1. Single crystal X-ray structure of the halogen-bonded co-crystal between N-ethyl-N-methyl-imidazolium iodide and n-C8F17-I (1:2 adduct).

Mono and diiodoperfluoroalkanes are key intermediates [1] for the synthesis of various fluorochemicals and fluoropolymers, such as fluorinated elastomers [2–4]. More recently these fluorous compounds have found applications in crystal engineering and supramolecular chemistry as robust tectons for halogen bond-driven self-assembly processes. Covalently bonded halogen atoms, in fact, show a highly asymmetric electron distribution resulting in an electron rich belt perpendicular to the covalent bond and an electron poor cap (σ-hole) [5] on its elongation. Both electron-poor and electron-rich sites can thus interact attractively with halogen atoms. The interaction involving halogens and electron-rich sites is known as halogen bond [6]. Due to the strong electron withdrawing properties of perfluorocarbon residues, the σ-hole on the heavier halogens in haloperfluorocarbons is particularly positive and the halogen bond formed by haloperfluorocarbons is, thus, an excellent supramolecular synthon. In this lecture it will be described how the hierarchical organization of molecular components into heteromeric solid architectures can be designed and realized through a cooperative interplay of the strong halogen bond given by the heavier halogen atoms of iodo- and bromoperfluorocarbons and the unique aggregation features of their perfluorocarbon skeletons [7,8].

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## C1.1

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# Competitive Adsorption of Phospholipids and Proteins at an Air/Water Interface: A Fluorocarbon Gas Can Boost its Kinetics

**P.N. NGUYEN [a], G. WATON [a], T. VANDAMME [b], M.P. KRAFFT [a]***

[a] Institut Charles Sadron (CNRS) University of Strasbourg - STRASBOURG (FRANCE)
[b] Faculty of Pharmacy University of Strasbourg - ILLKIRCH (FRANCE)

* krafft@unistra.fr

We report on the competitive adsorption of dipalmitoylphosphatidylcholine (DPPC) and bovine serum albumin (BSA) at the surface of a gas bubble submitted for sufficiently long sinusoidal oscillations at frequencies close to those encountered in respiration. We found that DPPC can then totally displace BSA from the interface.[1] The periodical surface variations dramatically accelerate the adsorption kinetics of the phospholipid; induce a dilute-to-condensed phase transition in the interfacial film; and permanently decrease the interfacial tension.[2] In the absence of oscillations, BSA is rapidly adsorbed at the interface, hindering the access of DPPC. We show that application of prolonged periodical variations, in the 7 to 50 s period range, thus provides a convenient tool for investigating, and possibly counteracting, the inhibitory effect of BSA towards phospholipid adsorption at an interface.

We further show that the kinetics of expulsion of BSA by DPPC can be increased by an order of magnitude by introducing a fluorocarbon in the bubble's gas phase. Previous studies have established that fluorocarbons can greatly facilitate DPPC re-spreading in Langmuir monolayers and prevent the deleterious effect of BSA penetration in these monolayers.[3-8] We have also established that fluorocarbons, when part of the bubble's gas phase, dramatically lower the equilibrium interfacial tension of phospholipids, hence playing the unexpected role of a co-surfactant.[9, 10] Our results should provide means for counteracting the potent lung surfactant inactivating effect of BSA.

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## C1.2

# Chemical linkage of perfluoropolyether chains to carbon-based nanomaterials: recent results and new perspective

**M. SANSOTERA** [a]*, **S. TALAEEMASHHADI** [a], **M. GOLA** [a], **C. BIANCHI** [b], **P.A. GUARDA** [c], **W. NAVARRINI** [a]

[a] POLITECNICO DI MILANO, FLUORITECH - MILANO (ITALY)
[b] UNIVERSITA DEGLI STUDI DI MILANO - MILANO (ITALY)
[c] Solvay Specialty Polymers - BOLLATE (ITALY)

* maurizio.sansotera@polimi.it

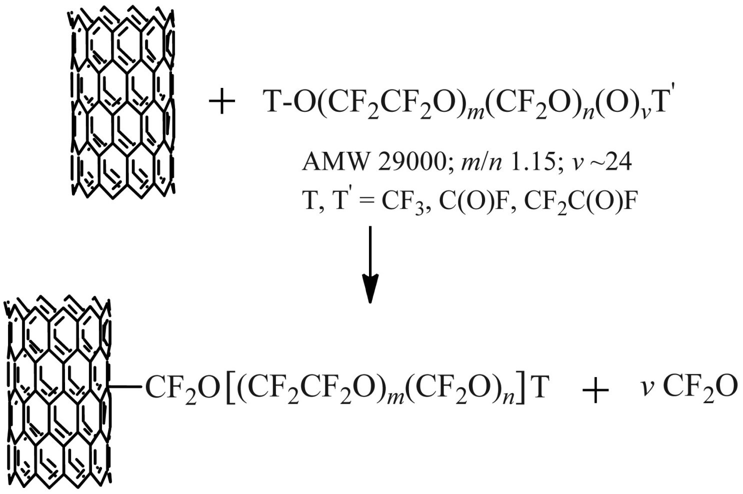

*Fig. 1. Functionalization of MWCNTs with linear PFPE peroxide.*

The science and application of carbonaceous nanostructures is quickly under development. The great interest on this class of molecules is due to the distinctive properties of carbonaceous nanomaterials which arise from the union of the unique features of sp2 hybridized carbon bonds and the unusual characteristics of physics as well as chemistry at the nanoscale level. Accordingly, the functionalization of carbonaceous nanomaterials opens a wide range of opportunities for altering their structural and electronic properties and affords new types of carbon-based materials with useful properties of their own. On the basis of our experience on functionalization of carbonaceous materials with perfluoropolyether (PFPE) peroxides [1], we started to approach the chemical linkage of PFPE chains also to carbon-based nanomaterials. As first result, superhydrophobic conductive multi-walled carbon nanotubes (MWCNTs) were prepared by thermal decomposition of the PFPE peroxide [2]. Reactive PFPE radicals were generated in the reaction environment and they reacted with the unsaturated moieties on MW-CNT surface. The PFPE-modified MW-CNTs were characterized by XPS, TGA, XRD, SEM and measurements of contact angle, surface area as well as resistivity at different applied pressures. New perspectives and preliminary results on functionalization of single-walled carbon nanotubes (SW-CNTs), fullerenes and graohebne by covalent linkage of PFPE chains are also discussed.

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## C1.3

# Exploring Conformational Space: Stereoelectronic Effects for the Design of Nematic Liquid Crystals

**P. KIRSCH** [(a)]*

[(a)] MERCK KGAA, LIQUID CRYSTAL R&D CHEMISTRY - DARMSTADT (GERMANY)

* peer.kirsch@merckgroup.com

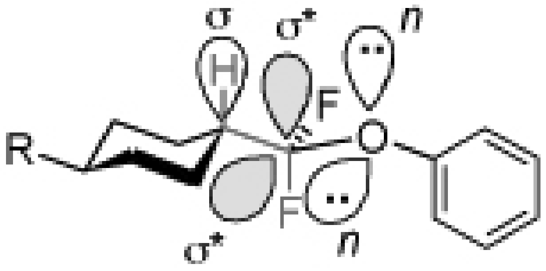
The majority of liquid crystals for LCD applications which were developed over the past decade contains fluorine not only as polar substituent on aromatic moieties but also as a part of aliphatic substructures [1,2]. These bridge elements often induce highly favorable, application-relevant properties such as high clearing temperature ($T_{NI}$), wide nematic phase range and low rotational viscosity ($g_1$).

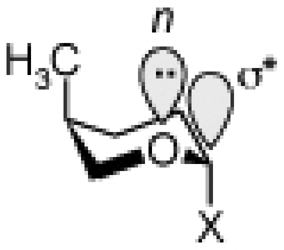
Of particular importance is the difluorooxymethylene ($CF_2O$) bridge [3]. Liquid crystals with this structural element are used in most modern touchpanel LCDs. Main cause of their unique property profile is the rigidification of the bridge by fluorine-induced stereoelectronic effects (“*gauche* effect”) [4].

Similar effects are also employed in order to rigidify otherwise flexible alkyl side chains of liquid crystals, resulting not only in elevated clearing points but also in negative dielectric anisotropy (De) [5].

However, stereoelectronic effects of strongly electronegative substituents have not always positive consequences for the design of liquid crystals. An analogue to the well-known “anomeric effect” in carbohydrates precludes the combination of certain building blocks in direct vicinity within the same mesogenic core structure [6].

Recent computational studies outline the limits of using stereoelectronic effects for controlling shape and rigidity of liquid crystals.





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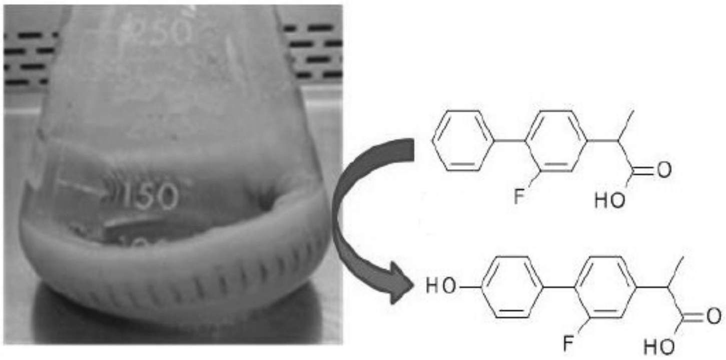
## IL-C2

# Biofilm-catalysed transformation of organofluorine compounds

**C. MURPHY** [(a)]*

[(a)] UNIVERSITY COLLEGE DUBLIN, BIOMOLECULAR AND BIOMEDICAL SCIENCE - DUBLIN (IRELAND)

* cormac.d.murphy@ucd.ie



*Biofilm-catalysed transformation of flurbiprofen*

Biofilms are microorganisms that grow attached to surfaces over which liquid flows. They are stable structures that have increased tolerance to xenobiotic compounds. Although often associated with infection and biofouling, biofilms offer the possibility of continuous biocatalytic transformation of pollutants and industrially relevant compounds. *Pseudomonas* biofilms have been established in membrane aerated and tubular reactors that employ fluoroacetate and fluorobenzoate as sole carbon sources, and can be operated over extended time periods. Biofilm of the filamentous fungus *Cunninghamella elegans* has recently been established, which can transform the fluorinated drugs flurbiprofen and flutamide to hydroxylated products, and could be employed for biological production of valuable fluorinated drug metabolites.

# TUESDAY, JULY 23

# TUESDAY, JULY 23

## Morning 9:00 – 10:30

## STREAM A

CHAIR: B. CROUSSE, *Faculté de Pharmacie Université Paris Sud (France)*

9:00 IL-A3 **Invited Lecture**
**HETEROATOM TRIFLUOROMETHYLATION**
**A. Togni**
*ETH Zurich, Dept of Chemistry (Switzerland)*

9:30 A3.1 **COPPER-CATALYZED AROMATIC TRIFLUOROMETHYLATION VIA β-CARBON ELIMINATION**
**H. Amii**
*Gunma University, Dept. of Chemistry & Chemical Biology, Gunma (Japan)*

9:50 A3.2 **TRIFLUOROMETHYLATION AND TRIFLUOROMETHYLTHIOLATION: NEW METHODS AND NEW REAGENTS**
**Q. Shen**
*Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, Shanghai (China)*

10:10 A3.3 **PENTAFLUOROETHYLATION OF ORGANIC COMPOUNDS WITH $(C_2F_5)_3P$ AND $(C_2F_5)_3P{=}O$ REAGENTS**
**N. Ignatiev**, H. Willner, A. Miller
*Merck KGaA, PM-ABE, Darmstadt (Germany)*

## STREAM B

CHAIR: R. HAGIWARA, *Kyoto University (Japan)*

9:00 IL-B3 **Invited Lecture**
**$XeF_2$: INTERESTING LIGAND IN COORDINATION COMPOUNDS AND USEFUL OXIDIZING AGENT**
**M. Tramšek,** E. A. Goreshnik, G. Tavcar, B. Žemva
*Jožef Stefan Institute, Dept of Inorganic Chemistry & Technology, Ljubljana (Slovenia)*

9:30 B3.1 **CATALYTIC HYDRODEFLUORINATION OF FLUOROMETHANES AT ROOM TEMPERATURE BY SILYLIUM-ION LIKE SURFACE SPECIES**
**M. Ahrens**, G. Scholz, A. Siwek, T. Braun, E. Kemnitz
*Humboldt-Universität, Dept of Chemistry Berlin (Germany)*

9:50 B3.2 **AEROGELS BASED ON $AlF_3$: DIRECT PREPARATION, NANOSTRUCTURE, AND SOME SURFACE CHARACTERISTICS**
A. Štefancic, D. Primc, **T. Skapin**
*Jožef Stefan Institute, Dept of Inorganic Chemistry & Technology, Ljubljana (Slovenia)*

10:10 B3.3 **PROBING THE CATALYTIC PROPERTIES OF $MgF_2$ PARTICLES. A THEORETICAL INVESTIGATION**
**E. Kanaki**, C. Müller, B. Paulus
*Institut für Chemie und Biochemie, Physical & Theoretical Chemistry, Berlin (Germany)*

# STREAM C

**CHAIR:** **M.P. KRAFFT**, ***Institut Charles Sadron (France)***

9:00 IL-C3 **Invited Lecture**
**SURFACE STRUCTURE AND WETTING BEHAVIOR OF FLUOROACRYLATE POLYMERS**
**A. Takahara**
*Kyushu University, Institute for Materials Chemistry & Engineering, Fukuoka (Japan)*

9:30 C3.1 **SUPERHYDROPHOBIC FLUORINATED SURFACES AND COMPARISON WITH THEIR HYDROCARBON ANALOGUES**
**M. Wolfs**, T. Darmanin, F. Guittard
*Université de Nice Sophia Antipolis & CNRS, LPMC - UMR 7336 (France)*

9:50 C3.2 **EFFICIENT MINERALIZATION OF FLUORINATED IONIC LIQUID ANIONS USING SUBCRITICAL AND SUPERCRITICAL WATER**
**H. Hori**, A. Takahashi, Y. Noda, T. Sakamoto
*Kanagawa University, Faculty of Science, , Hiratsuka (Japan)*

10:10 C3.3 **POROUS MATERIALS TEMPLATED BY FLUORINATED SURFACTANT-BASED SYSTEMS**
**J. Blin**, M.J. Stébé
*Université de Lorraine, Structure et Réactivité des Systèmes Moléculaires, Vandoeuvre Les Nancy (France)*

10:30 – 11:00 *Coffee*

## Morning 11:00 – 12:50

# STREAM A

**CHAIR**: **T. YAMAZAKI**, ***Tokyo University of Agriculture & Technology (Japan)***

| | | |
|---|---|---|
| **11:00** | **IL-A4** | **Invited Lecture**<br>**FLUORINE-CONTAINING AMINO PHOSPHONATES. A FAMILY OF BIOACTIVE MOLECULES**<br>**V. Kukhar**<br>*Institute of Bioorganic Chemistry & Petrochemistry, NAS of Ukraine, Fine Organic Synthesis, Kiev (Ukraine)* |
| **11:30** | **A4.1** | **FLUORINATED BASIC PANCREATIC TRYPSIN INHIBITOR**<br>**S. Ye**, A. A. Berger, B. Koksch<br>*FU Berlin, Institute of Chemistry & Biochemistry (Germany)* |
| **11:50** | **A4.2** | **BACKBONE-FLUORINATED AMINO ACIDS: SYNTHESIS AND APPLICATIONS**<br>**L. Hunter**<br>*The University of New South Wales, School of Chemistry, Sydney (Australia)* |
| **12:10** | **A4.3** | **A $^{19}F$ NMR LABEL TO SUBSTITUTE POLAR AMINO ACIDS IN PEPTIDES: A $CF_3$-SUBSTITUTED ANALOGUE OF SERINE AND THREONINE**<br>**A. Tkachenko**, P. Mykhailiuk, S. Afonin, D. Radchenko, V. Kubyshkin, A. Ulrich, I. Komarov<br>*ENAMINE Ltd, Kiev (Ukraine)* |
| **12:30** | **A4.4** | **MULTIGRAM-SCALE SYNTHESIS OF ENANTIOPURE TRIFLUOROMETHYLPYRROLIDINES: APPLICATION TO THE SYNTHESIS OF 5-TRIFLUOROMETHYLPROLINE**<br>**J. Pytkowicz**, H. Lubin, G. Chaume, T. Brigaud<br>*Université de Cergy-Pontoise, Laboratoire SOSCO, (France)* |

# STREAM B

**CHAIR**: **T. SKAPIN**, ***Jožef Stefan Institute, Ljubljana (Slovenia)***

| | | |
|---|---|---|
| **11:00** | **IL-B4** | **Invited Lecture**<br>**CARBON NANO-MATERIALS FOR ELECTRIC DOUBLE LAYER CAPACITANCE**<br>**Y. S. Lee**<br>*Chungnam National University, Dept. of Fine Chemical Engineering & Chemistry, Daejeon (Republic of Korea)* |

**11:30** **B4.1** **ELECTROLYTIC SYNTHESIS OF NITROGEN TRIFLUORIDE FROM A MOLTEN $NH_4F$•2HF MELT USING STEAM-ACTIVATED BORON-DOPED DIAMOND ELECTRODE**
**T. Goto**, A. Ooishi, Y. Sakanaka, W. Sugimoto, T. Nakai, M. Uno, K. Hirano, M. Saito, M. Inaba, A. Tasaka
*Doshisha University, Dept of Environmental Systems Science, Kyotanabe, Kyoto (Japan)*

**11:50** **B4.2** **SURFACE FLUORINATION OF YTTRIA STABILIZED ZIRCONIA NANOPARTICLES: TRANSFORMATION FROM OXIDE TO OXYFLUORIDE**
**O. Gorban**, S. Synyakina, G. Volkova, V. Glazunova, I. Danilenko, T. Konstantinova
*Donetsk Institute For Physics & Engineering of The NAS of Ukraine, Materials Science Dept, Donetsk (Ukraine)*

**12:10** **B4.3** **MAS NMR STUDY OF THE SOLIDIFIED CRYOLITE SYSTEMS WITH FeO ADDITION**
**F. Šimko**
*Institute of Inorganic Chemistry, Dept. of Molten Salts, Bratislava (Slovakia)*

**12:30** **B4.4** **TETRAFLUOROBROMATES FOR URBAN MINING OF NOBLE METALS – A CASE STUDY ON IRIDIUM METAL**
**S. Ivlev**, P. Woidy, F. Kraus, V. Shagalov, I. Gerin, R. Ostvald
*Tomsk Polytechnic University, Tomsk (Russia)*

## STREAM C

**CHAIR**: **D. DESMARTEAU, *Clemson University, Anderson (USA)***

**11:00** **IL-C4** **Invited Lecture**
**FLUOROPOLYETHER ELASTOMERS HAVING LOW GLASS TRANSITION TEMPERATURES**
S. Corveleyn, G. Mike, W. Grootaert, T. Opstal, G. Dahlke, **R. Dams**
*3M Belgium, Material Resource Division -R&D, Zwijndrecht (Belgium)*

**11:30** **C4.1** **SUSPENSION POLYMERIZATION KINETICS OF TFE**
**P. Crouse**, M. Mabudafhasi, T. Kili, J. Van Der Walt, C. Thompson
*University of Pretoria, Department of Chemical Engineering, Pretoria (South Africa)*

**11:50** **C4.2** **SYNTHESIS OF NOVEL PERFLUORINATED SULFONYL AZIDES AND PARTIALLY FLUORINATED ALKYL AZIDES AS NEW CROSSLINKING AGENTS FOR FLUOROPOLYMERS**
**I. Wlassics**, A. Marrani, V. Tortelli, I. Falco
*Solvay Specialty Polymers Italy SPA, New Fluorinated Materials - R&D, Bollate, Milano (Italy)*

**12:10** **C4.3** **SYNTHESIS OF FLUORINE-CONTAINING WATER-SOLUBLE POLYMERS AND STUDY OF THEIR TEMPERATURE-RESPONSIVE BEHAVIOURS**
**T. Irita**, T. Nagai, K. Adachi, S. Kanaoka, S. Aoshima
*Daikin Industries, Ltd., Chemical R&D Centre, Settsu-Shi-Osaka (Japan)*

**12:30** **C4.4** **SURFACE TREATMENT ON POLYMER PACKAGING FILMS USING VARIOUS FLUORINATION ROUTES**
**J. Peyroux**, M. Dubois, E. Tomasella, A. P. Kharitonov, D. Flahaut
*Institut de Chimie Clermont-Ferrand, Mat. Inorg. (France)*

**12:50 – 14:00** *Lunch*

## Afternoon 15:00 – 18:00

**On Tuesday July 23, the Exhibition on Henri Moissan will be transferred to Maison de la Chimie**

## MOISSAN SESSION AT « MAISON DE LA CHIMIE »

**CHAIR**: **G. FEREY,** *President of the International Advisor Board of the 17th ESFC, Member of the French Academy of Sciences*

**1.** Opening Ceremony (President B. Bigot)
**2.** Lectures of Moissan Prize Awardees *(25min each)*
   - **IL-M1** - **CHEMICAL SYNTHESIS OF ELEMENTAL FLUORINE,** by K. O. Christe, *University of Southern California, Loker Research Institute, Los Angeles, CA (USA)*
   - **IL-M2** - **MY FAVORITE MOLECULES,** by D. DesMarteau, *Clemson University, Dept Chemistry, Anderson, SC (USA)*
   - **IL-M3-** **THE IMPORTANCE OF FLUORINE IN CATALYSIS WITH ORGANOMETALLIC FLUORIDES AND IN COMPOUNDS WITH LOW VALENT MAIN GROUP ELEMENTS,** by H. Roesky, *University of Göttingen, Dept. of Inorganic Chemistry (Germany)*
   - **IL-M4-** **SYNTHESIS AND PHYSICAL CHEMICAL PROPERTIES OF INORGANIC FLUORIDES: "FROM SINGLE CRYSTALS TO FUNCTIONALIZED NANOFLUORIDES,** by A. Tressaud, *ICMCB-CNRS, Bordeaux-Pessac (France)*

**3.** Presentation by President B. Bigot and Dr G. Férey of the 2012 Moissan Prize
**4.** Presentation by M. Nappa and M. Pabon of the *International Young Talent Award in Fluorine Chemistry*, sponsored by DuPont and commemorating the 75th Anniversary of the discovery of Teflon® by R. Plunkett
**5.** Preview of a movie on Henri Moissan (J. Trouchaud & D. Bour)

**18:00** **COCKTAIL & BANQUET**

# STREAM A

TUESDAY, JULY 23

## IL-A3

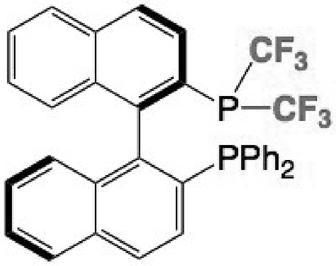
# Heteroatom Trifluoromethylation

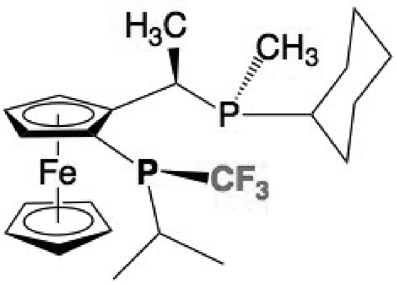
**A. TOGNI** [(a)]*

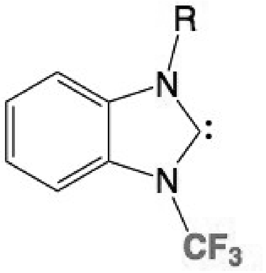
[(a)] Department of Chemistry and Applied Biosciences, ETH ZURICH - ZURICH (SWITZERLAND)

* atogni@ethz.ch

The lecture will address selected recent findings concerning the electrophilic trifluoromethylation of heteroatom substrates such as primary and secondary phosphanes [1,2] and azoles [3] using hypervalent iodine reagents [4]. These reactions are key to the syntheses of chiral ligands containing a stereogenic P-$CF_3$ group, or new NHC ligands having an electron-withdrawing trifluoromethyl substituent on nitrogen. Coordination chemical aspects and application in catalysis of the new ligands, e.g. in hydrogenation reactions, along with mechanistic studies, will be presented.







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## A3.1

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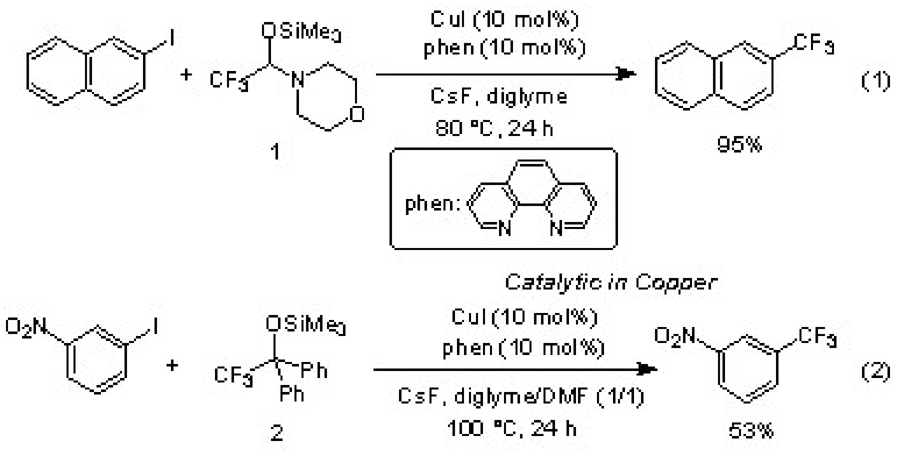
# Copper-Catalyzed Aromatic Trifluoromethylation via β-Carbon Elimination

**H. AMII** [(a)*]

[(a)] GUNMA UNIVERSITY, DEPARTMENT OF CHEMISTRY AND CHEMICAL BIOLOGY, GRADUATE SCHOOL OF ENGINEERING - KIRYU, GUNMA (JAPAN)

* amii@gunma-u.ac.jp

Trifluoromethylated aromatic compounds are the substances of considerable interest in various industrial fields. Owing to the increasing demands for fluoroaromatics, new methodologies for aromatic trifluoromethyla Trifluoromethylated aromatic compounds are the substances of considerable interest in various industrial fields. Owing to the increasing demands for fluoroaromatics, new methodologies for aromatic trifluoromethylation have been required from the viewpoints of cost, simplicity, efficiency, versatility, and environmental benignity including a catalytic process [1]. In 2009, we reported the first successful example of aromatic trifluoromethylation using a diamine ligand which makes possible a reaction catalytic in copper [2]. A small amount of CuI-phenanthroline complex engendered the cross-coupling reactions of aryl/ heteroaryl iodides with $CF_3SiEt_3$ to give trifluoromethylated arenes. Herein, we present catalytic aromatic trifluoromethylation via beta-carbon elimination. Fluoral (trifluoroacetaldehyde) and its derivatives are readily available compounds. Hemiaminals of fluoral are known to be convenient sources of trifluoromethyl anion [3]. We developed a catalytic procedure for aromatic trifluoromethylation by the use of trifluoroacetaldehyde hemiaminal derivative 1 as a cross-coupling partner (eq 1) [4]. Furthermore, the cross-coupling reactions employing carbinol 2 will be disclosed (eq 2).



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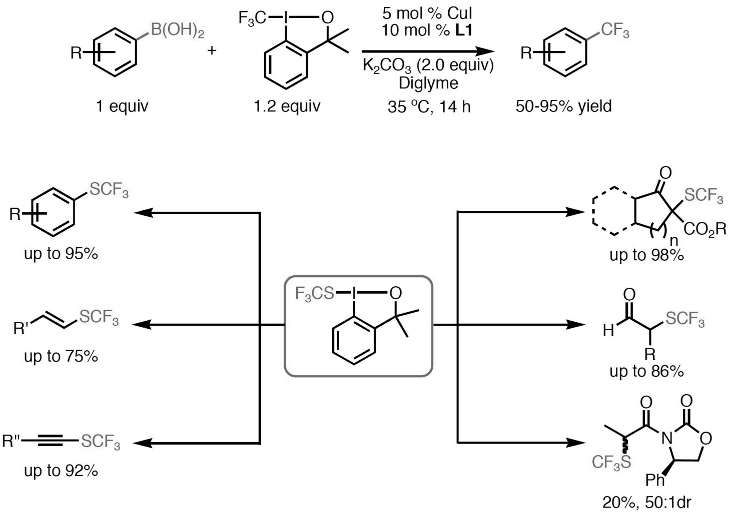
## A3.2

# Trifluoromethylation and Trifluoromethylthiolation: New Methods and New Reagents

**Q. SHEN** [(a)]*

[(a)] SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, KEY LABORATORY OF ORGANOFLUORINE CHEMISTRY,
CAS - SHANGHAI (CHINA)

* shenql@sioc.ac.cn



It is well known that the replacement of a hydrogen atom with fluorine in organic compounds brings significant biological and chemical changes. Among many fluorinated functional groups, the trifluoromethyl group ($CF_3$-) and trifluoromethylthio group ($CF_3S$-) are two of the most lipophilic substituents. In general, incorporation of trifluoromethyl or trifluoromethylthio group into small molecules greatly enhances its ability to cross lipid membranes and in vivo absorption rate. Moreover, ther high electronegativity of the two groups significantly improves the small molecule's stability in acidic environments. As a result, both trifluoromethyl and trifluoromethylthio group have been of special interest from pharmaceutical and agrochemical industry.Although several strategies employing transition-metal catalysts emerged for the preparation of trifluoromethyl- or trifluoromethylthio-substituted arenes in the past several years, the development of general catalytic methods for the incorporation of these two groups under mild conditions remains a challenge for synthetic organic chemists.

In 2011, we reported a copper-catalyzed protocol for trifluoromethylation of aryl and alkenylboronic acids with trifluoromethylated hypervalent iodine reagent (Togni's reagent). The reaction proceeded in good to excellent yields for a range of different substrates including heteroarylboronic acids and substrates with a variety of functional groups under mild reaction conditions. Inspired by these results, we envisioned that a trifluoromethylthiolated hypervalent iodine reagent would be a powerful electrophilic reagent for the introduction of trifluoromethylthio group. Herein, we present the invention of such a reagent and its reactions with a variety of nucleophiles such as b-ketoesters, aldehydes, amides, aryl or vinyl boronic acids or alkynes under mild conditions.

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## A3.3

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# Pentafluoroethylation of organic compounds with $(C_2F_5)_3P$ and $(C_2F_5)_3P{=}O$ reagents

**N. IGNATIEV** [(a)]*, **H. WILLNER** [(b)], **A. MILLER** [(b)]

[(a)] MERCK KGAA, PM-ABE - DARMSTADT (GERMANY)
[(b)] Bergische Universität Wuppertal, Anorganische Chemie - WUPPERTAL (GERMANY)

* nikolai.ignatiev@merckgroup.com

Trifluoromethylation of organic compounds by means of $(CH_3)_3SiCF_3$ or $CHF_3$ is well developed [1,2]. Pentafluoroethylation is much less studied. $C_2F_5I$, $(CH_3)_3SiC_2F_5$ and $C_2F_5Li$ as pentafluoroethylation reagents were investigated [3], but all these reagents have certain disadvantages.

Recently we have applied $(C_2F_5)_3P$ [4] and $(C_2F_5)_3P{=}O$ [5] reagents to pentafluoroethylate various organic compounds.

$(C_2F_5)_3P$ can be easily prepared by reduction of $(C_2F_5)_3PF_2$ (industrially available material [6,7]) with $NaBH_4$ [4]. $(C_2F_5)_3P{=}O$ can be obtained from $(C_2F_5)_3PF_2$ in different ways, *i.e.* by the reaction with $(CH_3)_3SiOSi(CH_3)_3$ [8], CaO [9], $SO_2$ or $SiO_2$ [10].

The application of $(C_2F_5)_3P$ and $(C_2F_5)_3P{=}O$ as reagents for pentafluoroethylation of organic compounds will be presented and discussed on the examples of benzophenone and $(CH_3O)_3B$. Synthesis of $K[C_2F_5BF_3]$ will be described.

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## IL-A4

# Fluorine-containing Amino Phosphonates. A Family of Bioactive Molecules

**V. KUKHAR** [(a)]*

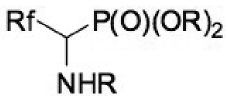
[(a)] INSTITUTE OF BIOORGANIC CHEMISTRY & PETROCHEMISTRY, NAS OF UKRAINE, FINE ORGANIC SYNTHESIS - KIEV (UKRAINE)

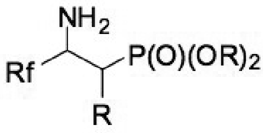
* kukhar@bpci.kiev.ua

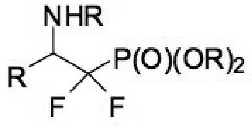
The fluorinated organophosphates and organophosphonates are other important area of natural phosphate mimics [1]. In general, incorporating fluorine as either a bioisosteric replacement for hydrogen or an isoelectronic replacement for the hydroxyl group has considerable impact on the behaviour of a phosphate in a biological environment. Many of the fluorinated phosphorus species are good enzyme inhibitors, very useful tools to obtain crucial information regarding the catalytic mechanism of enzymatic reactions.

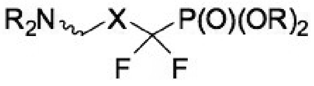
Introduction of fluorine atoms or fluoroalkyl groups with aminophosphonic acids, as structural analogous of the corresponding amino carboxylic derivatives [2], offers new interesting opportunities for significant changes of physical, chemical, and biological properties of the resulting molecules. The presence of fluorine atoms or fluoroalkyl groups can strongly affect functional properties of aminophosphonic acid derivatives, such as acidity and basicity of nearby functional groups. These structural features have resulted in the development of fluorinated aminophosphonates exhibiting antitumor, antibacterial, antiviral, insecticidal, and antifungal activities. Application of a large number of fluorinated aminophosphonic acid derivatives as enzyme inhibitors has also been demonstrated. Due to these promising applications in bioorganic chemistry, it is not surprising that development of synthetic methods allowing reliable, convenient access to fluorinated aminophosphonic acids and their derivatives, desirably in enantiomerically pure form to satisfy the need for systematic biological studies, is currently the subjects of intensive synthetic research activities.

In the report we will discuss the main tendencies and recent results in modern syntheses of fluorinated aminophosphonates.









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## A4.1

# Fluorinated basic pancreatic trypsin inhibitor

**S. YE** [(a)], **A.A. BERGER** [(a)], **B. KOKSCH** [(a)]*

[(a)] Freie Universität Berlin, Institute of Chemistry and Biochemistry - BERLIN (GERMANY)

* Beate.Koksch@fu-berlin.de

Proteins have shown great potential as highly active pharmaceuticals. Enhancing protein stability, biocompatibility and creating novel catalytic capability are major goals of protein engineering. In recently years, fluorine has emerged as a powerful tool in protein engineering.[1] Improvement of chemical and biological approaches such as solid-phase peptide synthesis, chemoselective peptide ligation, and protein expression containing non-canonical amino acids enable incorporation of fluorinated amino acids into protein site-specifically and residue-specifically.[2,3]

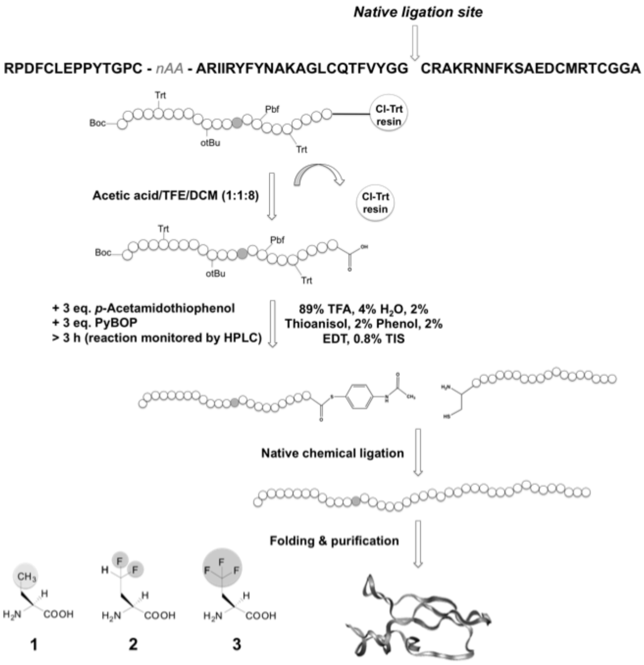

*Fig. 1. Schematic representation of synthesis strategy for mutant BPTIs and non-canonical amino acids used in this study.*

Herein we present the total chemical synthesis of basic pancreatic trypsin inhibitor (BPTI), in which Lys 15 ($P_1$ site) was substituted by non-canonical amino acids (*S*)-ethylglycine (Abu) and two of its fluorinated analogues, (*S*)-2-amino-4,4-difluorobutanoic acid (DfeGly) and (*S*)-2-amino-4,4,4-trifluorobutanoic acid (TfeGly).[4]The protein stability and inhibitory ability of mutant species were investigated.

Our data showed that the incorporation of DfeGly and TfeGly at the solution interface increased protein stability of BPTI while incorporation of Abu decreased its stability. Surprisingly, BPTIs containing fluorinated amino acids also showed high inhibitory ability.[5]

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## A4.2

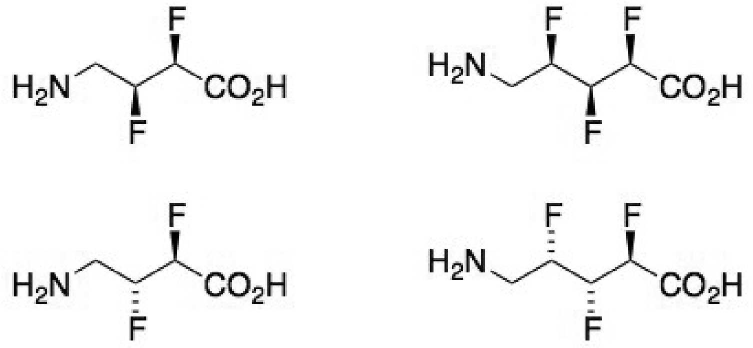
# Backbone-fluorinated amino acids: synthesis and applications

**L. HUNTER** [(a)]*

[(a)] THE UNIVERSITY OF NEW SOUTH WALES, SCHOOL OF CHEMISTRY - SYDNEY (AUSTRALIA)

* l.hunter@unsw.edu.au

The incorporation of fluorine atoms into organic molecules can have a dramatic impact on the substances' physical and chemical properties. For example, fluorine substituents can lead to higher hydrophobicity and greater metabolic stability, and they can affect the pKa of nearby functional groups. All of these effects have been put to good use in the pharmaceuticals arena: so much so, that approximately 20% of drugs currently on the market are organofluorine compounds.



*Backbone-fluorinated amino acids*

In addition to the effects described above, there is another impact of fluorine substitution that is less widely appreciated: fluorine atoms affect molecular conformation. The highly polarised C–F bond participates in a variety of stereoelectronic interactions with adjacent functional groups, and these interactions can favour certain molecular conformations over others. Thus, it is possible to rationally "program" molecules to adopt desired conformations by decorating them with carefully-designed patterns of fluorine substituents [1].

This presentation will describe the synthesis of fluorinated backbone-homologated amino acids (Figure 1). These molecules have been characterised by NMR, X-ray crystallography and molecular modelling, and it emerges that the different stereoisomers have very different preferred conformations [2]. Current work is focused on exploiting these shape-controlled molecules in a variety of biological contexts, including as GABA receptor ligands [3] and as components of anti-microbial and anti-angiogenic peptides [4,5].

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## A4.3

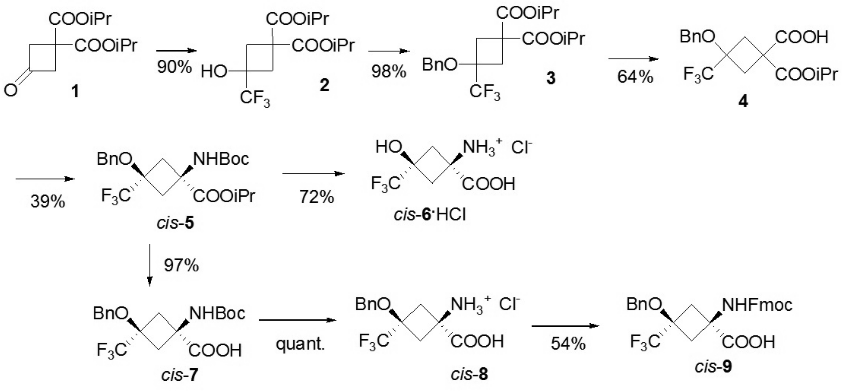
# A $^{19}$F NMR Label to Substitute Polar Amino Acids in Peptides: A $CF_3$-Substituted Analogue of Serine and Threonine

**A. TKACHENKO** [(a)*], **P. MYKHAILIUK** [(a)], **S. AFONIN** [(b)], **D. RADCHENKO** [(a)], **V. KUBYSHKIN** [(b)], **A. ULRICH** [(b)], **I. KOMAROV** [(a)]

[(a)] ENAMINE LTD, CHEMISTRY - KYIV (UKRAINE)
[(b)] Karlsruhe Institute of Technology - KARLSRUHE (GERMANY)

* antontk@bigmir.net

The cyclobutane scaffold was used to design the first polar nonperturbing rigid $CF_3$-substituted amino acid suitable for replacing the serine/threonine residues in peptides. This amino acid imitates the geometry, structure, and function of serine and threonine, but in contrast to those, it can be used in structural studies of membrane-active serine/threonine-containing peptides by solid-state $^{19}$F NMR



*synthetic scheme*

To validate the use of designed amino acid as a $^{19}$F-NMR label in structural studies, natural membrane-active antimicrobial peptide Temporin A (TA) was synthesized as a model compound. In a standard antimicrobial assay modified peptide displayed the same selectivity as the wild-type TA. Circular dichroism spectra showed that modified peptide adopts a random coil conformation in aqueous solutions but folds as a helix in membrane-mimetic environments. In solid state NMR experiment the peptide was readily reconstituted in oriented lipid bilayers, remained non-aggregated and demonstrated dipolar splitting useful for structural analysis.

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## A4.4

# Multigram-scale Synthesis of Enantiopure Trifluoromethylpyrrolidines: Application to the synthesis of 5-trifluoromethylproline

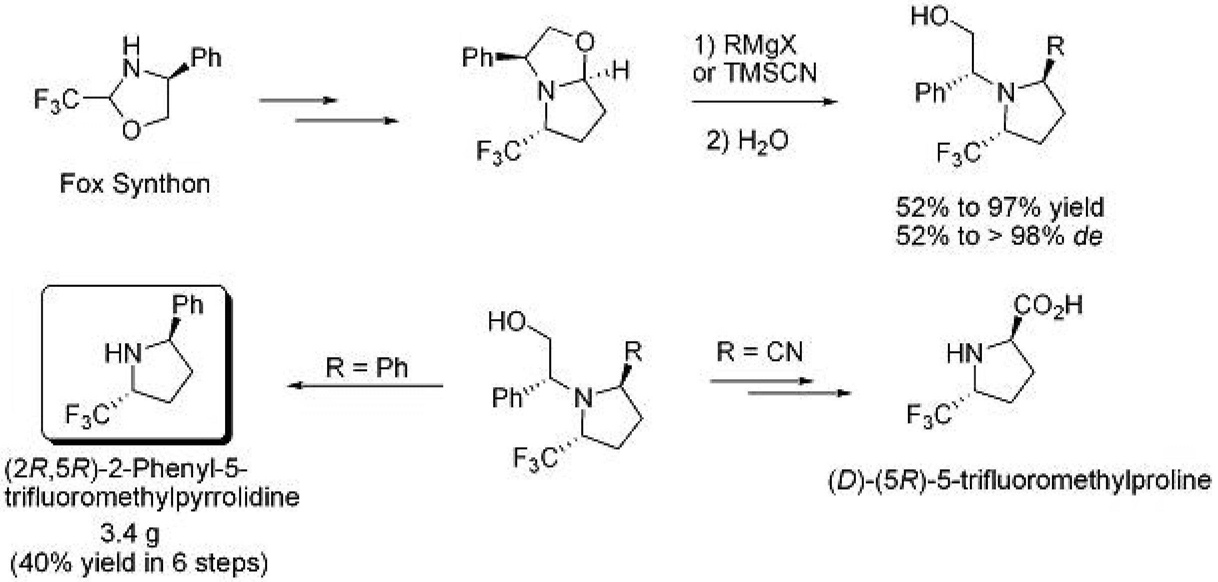
**J. PYTKOWICZ** [(a)]*, **H. LUBIN** [(a)], **G. CHAUME** [(a)], **T. BRIGAUD** [(a)]

[(a)] UNIVERSITE DE CERGY-PONTOISE, LABORATOIRE SOSCO - CERGY-PONTOISE (FRANCE)

* julien.pytkowicz@u-cergy.fr

Synthesis of chiral pyrrolidine derivatives is an important challenge for pharmaceutical applications and asymmetric synthesis. Although numerous methods were published for their preparation in the non fluorinated series,[1] the synthesis of chiral trifluoromethylpyrrolidine-type compounds is scarcely documented in the literature.[2] For example, the racemic synthesis of the *cis*-5-trifluoromethylproline was only reported very recently.[2h]

We will report the methodological study starting from a chiral trifluoromethyloxazolidine (Fox) synthon leading to the straightforward multigram-scale preparation of enantiopure (2*R*,5*R*)-2-phenyl-5-trifluoromethylpyrrolidine and (D)-(5*R*)-5-trifluoromethylproline. The key step of the strategy is respectively the addition of a Grignard reagent[1d] or a Strecker type addition on a bicyclic oxazolidine. (*scheme 1*)



*scheme 1*

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# STREAM B

## TUESDAY, JULY 23

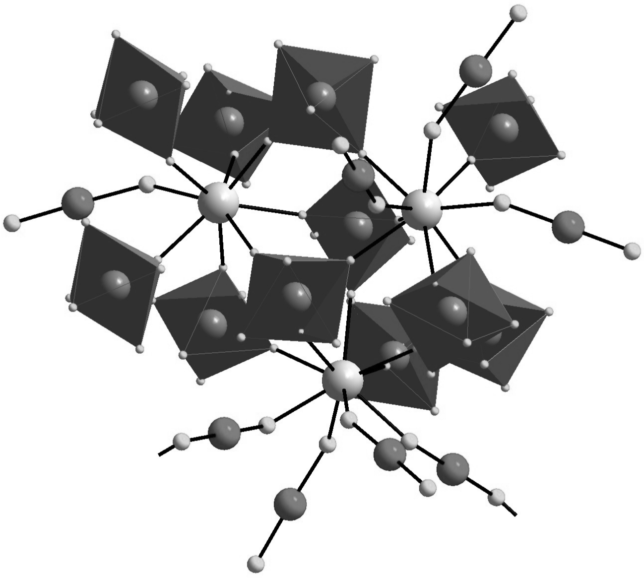
## IL-B3

# $XeF_2$: interesting ligand in coordination compounds and useful oxidizing agent

**M. TRAMŠEK** [(a)]*, **E.A. GORESHNIK** [(a)], **G. TAVCAR** [(a)], **B. ŽEMVA** [(a)]

[(a)] JOŽEF STEFAN INSTITUTE, DEPARTMENT OF INORGANIC CHEMISTRY AND TECHNOLOGY - LJUBLJANA (SLOVENIA)

* melita.tramsek@ijs.si



Coordination spheres of Ca centres

Two aspects of $XeF_2$ chemistry will be presented: its role as a ligand to metal centre and some of its oxidizing capabilities. In the course of the systematic attempts to oxidize Xe with $Ag(II)_{solv}$ in anhydrous HF (aHF), the first compound with $XeF_2$ a ligand to the metal centre, was prepared: $[Ag(XeF_2)_2](AsF_6)$.[1] Nearly decade later we started with systematic investigations of the reactions of various metal salts of the type $M^{n+}(AF_6^-)_n$ with $XeF_2$[2] in aHF solvent. More than forty compounds of the type $[M^n(XeF_2)_p](AF_6)_n$ were prepared and their crystal structures determined. The coordination sphere around metal cations in these coordination compounds is comprised of fluorine atoms from $XeF_2$ ligands and $AF_6^-$ anions or in some cases exclusively from $XeF_2$ ligands. Variety of structural types can be found: from molecular structure to three-dimensional network. In some cases compounds with two or even three metal centres with different coordination spheres were found. In the recently isolated and characterized $[Ca_3(XeF_2)_7](NbF_6)_6$ three different Ca atoms with completely different coordination spheres were found. $Xe_2F_3AF_6$ (A = Ru, Ir) were also used as starting materials for the preparation of the coordination compounds with $XeF_2$. For their preparation the oxidizing power of $XeF_2$ was employed. $XeF_2$ is capable of oxidizing ruthenium and iridium metals in aHF to Ru(V) and Ir(V) fluorides. Structures of $Xe_2F_3RuF_6 \cdot XeF_2$, $Xe_2F_3RuF_6$ and $Xe_2F_3IrF_6$ will be discussed.

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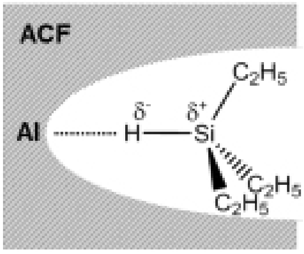
## B3.1

# Catalytic Hydrodefluorination of Fluoromethanes at Room Temperature by Silylium-ion like Surface Species

**M. AHRENS** [(a)*], **G. SCHOLZ** [(a)], **A. SIWEK** [(a)], **T. BRAUN** [(a)], **E. KEMNITZ** [(a)]
[(a)] Humboldt-Universität zu Berlin, DEPARTMENT OF CHEMISTRY - BERLIN (GERMANY)
* mike.ahrens@staff.hu-berlin.de

Breaking C−F bonds catalytically under moderate conditions is a fundamental challenge in synthetic chemistry. The conversions can provide new reaction pathways to otherwise not accessible fluorinated compounds and building blocks.



*Schematic representation of "ACF…H-SiEt3"*

Catalytic C−F bond activation reactions under mild conditions on using silylium-ions in combination with hydrogen sources like tertiary silanes have attracted great attention during the last years.[1] All reported reactions take place in the homogeneous phase, and voluminous weakly coordination anions (WCA) are needed to generate and stabilize the catalytically active silylium-ions. Up to date, C−F bond activation reactions using heterogeneous catalysts are restricted to gas phase methods at high temperatures.

Aluminum chlorofluoride (ACF)[2] and HS-$AlF_3$[3] are two of the strongest known solid Lewis acids and both are able to catalyze numerous reactions with fluoroorganic compounds. Regarding ACF, the abstraction of fluoride ions at the solid surface is considered to be the crucial step. Nevertheless, ACF was considered not to be active in hydrodefluorination (HDF) reactions.[4]

Recently, we found that ACF and HS-$AlF_3$ are both capable to catalyze H/D exchange reactions between deuterated alkanes and benzene.[5] Here, we present a strategy to use ACF and HS-$AlF_3$ as highly efficient heterogeneous C−F bond activation catalysts in the presence of tertiary silanes at room temperature and atmospheric pressure. For fluorinated methanes, C−F bonds can be converted into either C−H or C−C bonds with turn over numbers up to 400.[6]

The crucial step is the formation of a "ACF···H−$SiEt_3$" surface species (Fig. 1) with considerable silylium-ion character. Thus a method has been developed which opens up an opportunity for "silylium-ion chemistry on a solid surface".

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## B3.2

# Aerogels Based on $AlF_3$: Direct Preparation, Nanostructure, and Some Surface Characteristics

**A. ŠTEFANCIC [c], D. PRIMC [c], T. SKAPIN [c]***

[c] Jožef Stefan Institute, Dept. Inorg. Chem. & Technol. - LJUBLJANA (SLOVENIA)

* tomaz.skapin@ijs.si

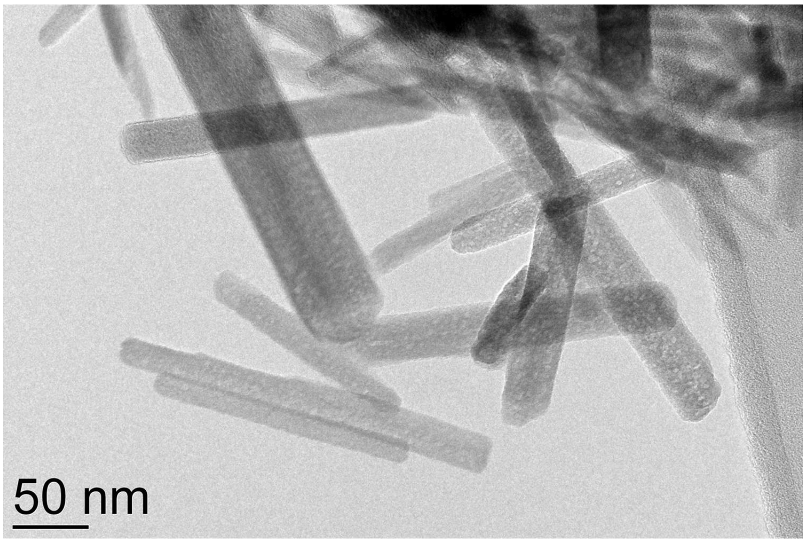

*Fig. 1. TEM micrograph of a typical $AlF_3$-based aerogel.*

Nanostructured inorganic solid fluorides with extraordinary high surface (HS) areas were the subject of intense investigations performed within the last ten years [1,2]. New preparation procedures developed in this period allowed the preparation of a variety of single and mixed solid fluorides with unprecedented characteristics that may be primarily associated with their distinctive nanostructure. In this context, we are investigating the possible direct preparation of aerogel-like fluorides that exhibit very high porosity. In the initial stage, work is focused on the preparation of $AlF_3$-based aerogels due to the demonstrated technical relevance of HS-$AlF_3$ and related materials [1,2].

With a modified fluoride sol-gel process [1], solutions of $Al(O^iPr)_3$ in various polar and non-polar organic solvents are converted to fluoride sols, gels or suspensions, by the addition of aHF. Wet fluoride precursors are afterwards dried, usually at supercritical conditions. Preliminary account of these procedures was given recently [3]. Typical aerogels, with very voluminous bulk structures and with specific surface areas in the range of 60–130 $m^2\ g^{-1}$, are obtained only with MeOH-containing liquid phases. Other combinations of organic solvents give partially collapsed powdery products with considerably lower surface areas of 30–40 $m^2\ g^{-1}$. SEM and TEM reveal that $AlF_3$-based aerogels consist of unisometric particles (nanorods) that are 5–20 nm wide and 100–300 nm long, and are loosely entangled in very open aerogel structures (Fig. 1). XRD indicates the formation of crystalline β-$AlF_3$ with a HTB-type structure; compositions deduced from other data are however closer to $AlF_{3-x}(OH)_x \cdot yH_2O$ (x<0.2) that may be associated with partial hydrolysis. Role of the very stable surface methoxy groups, that appear to be crucial in the formation of bulk aerogel structures and remain strongly bound to surface active sites, will be discussed.

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## B3.3

# Probing the catalytic properties of $MgF_2$ particles. A theoretical investigation.

**E. KANAKI** [(a)]*, **C. MÜLLER** [(b)], **B. PAULUS** [(b)]

[(a)] Institut für Chemie und Biochemie, FU Berlin, Physikalische und Theoretische Chemie - BERLIN (GERMANY)
[(b)] Institut für Chemie und Biochemie, FU Berlin - BERLIN (GERMANY)

* kanaki@chemie.fu-berlin.de

Magnesium fluoride based nanomaterials show promising results in the field of heterogeneous catalysis [1]. A recently developed sol-gel procedure [2] enables surface modification during synthesis of the nanomaterial, and thus, adjustment of the catalytic properties, by varying $H_2O$ and HF concentration. However, the mechanistic complexity of the procedure, and the nature of the nanomaterial makes a direct characterization difficult, if not impossible.

Combining density functional theory (DFT) and surface thermodynamics, we provide a tool for predicting the nanoparticles' morphology depending on the synthetic conditions. For this purpose, surface energies of low index surfaces with different terminations, substitution patterns and adsorbates are calculated and compared. Assuming a thermodynamic equilibrium between the $MgF_2$ bulk, $H_2O$ and HF we create, for selected temperatures, phase diagrams for each surface in a mixed HF and $H_2O$ environment. Based on these, we use Wulff construction to predict the most favorable shape of $MgF_2$ particles.

In addition, the calculation of the adsorbates' IR vibrational frequencies allow for a characterization of all exposed surfaces. The activity of Lewis acidic sites on the surface is evaluated through the shift of the vibrational frequencies of adsorbed CO which allows us to relate our results to experiment.

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## IL-B4

# Carbon nano-materials for electric double layer capacitance

**Y.S. LEE** [(a)]*

[(a)] CHUNGNAM NATIONAL UNIVERSITY, DEPT. OF FINE CHEMICAL ENGINEERING AND CHEMISTRY - DAEJEON (REPUBLIC OF KOREA)

* youngslee@cnu.ac.kr

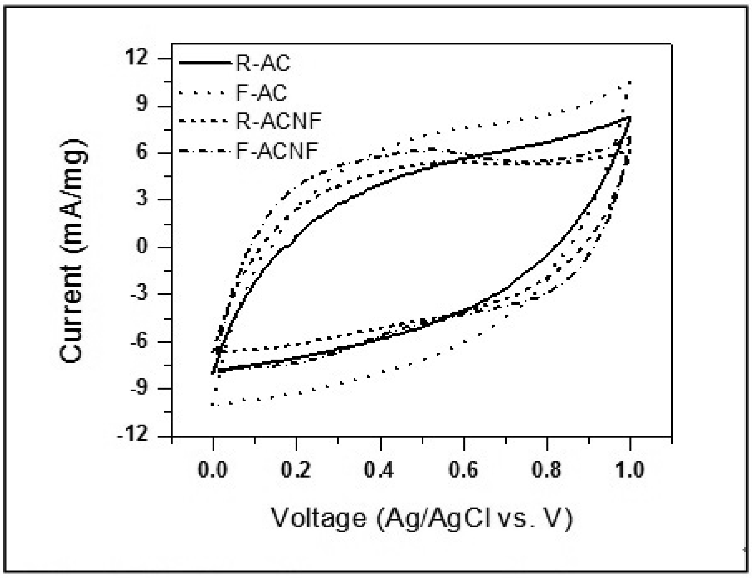

*Fig. 1. Cyclic voltammograms of carbon nano-materials obtained at 50 mV/s.*

Electric double layer capacitors (EDLC) are a promising technology for energy storage devices in electronic applications [1]. Many researches were issued in EDLC for increasing the specific capacitance. Theoretically, specific capacitance of EDLC is increased increasing specific area of the active materials. Specific capacitance is affected by both the specific surface area and pore properties. However, it is difficult to increase the specific surface area of the active materials while maintaining its porous structure. Because the performance of an EDLC is based on the accumulation of charge at the electrode/electrolyte interface, the surface characteristics of the active materials are very important [2]. Therefore, the surface modification of the AC is crucial to the improvement of EDLC capacity. So, in this study, the surface of a carbon nano-materials used as an electrode in an EDLC was modified via fluorination methods for investigation of capacitance. Two types of carbon nano-materials were used to investigate fluorination effect on the electrochemical properties; activated carbons (ACs) and activated carbon nanofiber (ACNFs). The changes of surface functional groups of fluorinated carbon nano-materials were investigated by XPS. And the pore structure of samples was assessed by N2 adsorption at liquid nitrogen temperature. Cyclic voltammetry (CV) of the fluorinated carbon nano-material-based EDLC was measured in a 1 M H2SO4 electrolyte. The specific capacitances of carbon nano-materials increased significantly after fluorination. At Fig. 1, the specific capacitance of fluorinated AC increased from 145 F/g to 212 F/g with the scan rates of 50 mV/s, in comparison to these of an unfluorinated ACs. The specific capacitance of fluorinated ACNFs also increased from 150 F/g to 179 F/g with the scan rates of 50 mV/s, in comparison to these of an unfluorinated ACNFs. This enhancement in capacitance can be attributed that the introduction of C-F functional groups onto the carbon nano-material surface was more important than the induction of changes in the textural properties of the carbon nano-materials with respect to improving the electrochemical properties of the carbon nano-materials. These results demonstrate that a fluorinated nanocarbon effectively enhances specific capacitance of EDLC.

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## B4.1

# Electrolytic synthesis of nitrogen trifluoride from a molten $NH_4F•2HF$ melt using steam-activated boron-doped diamond electrode

**T. GOTO** [(a)]*, **A. OOISHI** [(b)], **Y. SAKANAKA** [(a)], **W. SUGIMOTO** [(c)], **T. NAKAI** [(d)], **M. UNO** [(d)], **K. HIRANO** [(d)],
**M. SAITO** [(b)], **M. INABA** [(b)], **A. TASAKA** [(b)]

[(a)] Department of Environmental Systems Science, Doshisha University - KYOTANABE (JAPAN)
[(b)] Department of Molecular Chemistry and Biochemistry, Graduate School of Engineering, Doshisha University - KYOTANABE (JAPAN)
[(c)] Faculty of Textile Science, Shinshu University - UEDA (JAPAN)
[(d)] Permelec Electrode LTd. - FUJISAWA (JAPAN)

* tgoto@mail.doshisha.ac.jp

Electrolytic production of $NF_3$ in industry is currently conducted in a molten $NH_4F•2HF$ melt using a nickel anode. However, a relatively high corrosion rate of the nickel anode is one of the problems in this method. In order to overcome this drawback, we have selected a boron-doped diamond (BDD) as a new anode in the severe fluorination conditions for practical use, since a BDD is physically and chemically stable. We have already reported the possibility of a BDD as a new anode.In this study, to prolong durability of a BDD as an anode, steam-activated was conducted for improving surface properties of a BDD electrode and the performance of the steam-activated BDD electrode for $NF_3$ current efficiency was investigated.Anode potential on the steam-activated BDD electrode was lowered than that on the BDD electrode without steam activation during electrolysis at 100 mA $cm^{-2}$ for 100 h. However, SEM observation and XRD analysis of the fractured surface of the electrode revealed that the diamond structure on the BDD anode was maintained after the electrolysis for 800 h. The destruction of BDD anode was partially caused by permeation of HF in a melt through pores formed on the surface of BDD electrode during pre-treatment of steam activation. In order to avoid the pores formation, a grassy carbon was used instead of FE-5 carbon, as a substrate of the BDD electrode. The performance of electrolytic production of $NF_3$ using the steam-activated BDD on a glassy carbon substrate was successfully improved, and hence it is concluded that the steam-activated BDD electrode with a grassy carbon substrate is one of the good candidates as the anode for electrolytic production of $NF_3$.

## B4.2

# Surface fluorination of yttria stabilized zirconia nanoparticles: transform from oxide to oxyfluoride

**O. GORBAN** [(a)]*, **S. SYNYAKINA** [(b)], **G. VOLKOVA** [(b)], **V. GLAZUNOVA** [(b)], **I. DANILENKO** [(b)], **T. KONSTANTINOVA** [(b)]

[(a)] DONETSK INSTITUTE FOR PHYSICS AND ENGINEERING OF THE NAS OF UKRAINE, MATERIALS SCIENCE DEPARTMENT - DONETSK (UKRAINE)
[(b)] DONETSK INSTITUTE FOR PHYSICS AND ENGINEERING OF THE NAS OF UKRAINE - DONETSK (UKRAINE)

* oxanag1@ukr.net

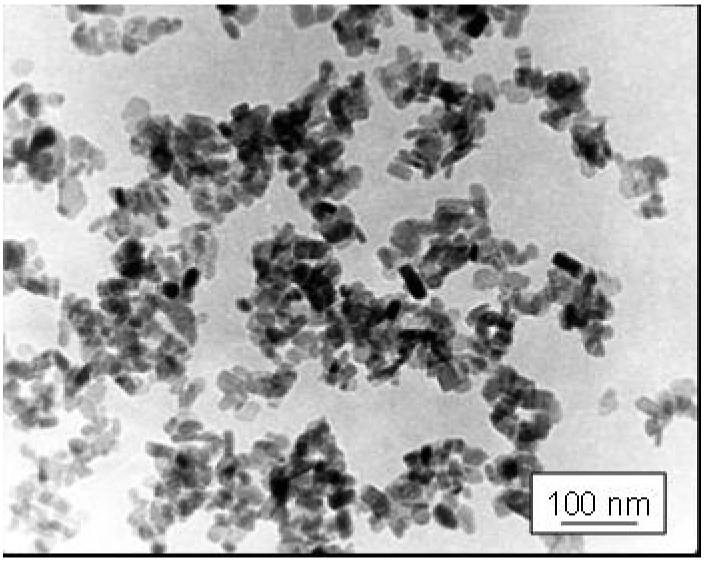

*Fig. 1. Surface fluorination yttria stabilized zirconia nanoparticles (700C)*

The surface fluorination of yttria stabilized zirconia nanoparticles is part of many technologies of functional materials for medicine and industry. The surface fluorination of zirconia nanopowders is used to improve the adhesion between ceramic implant and living tissue or between nanoparticles and polymeric matrix of composite materials in medicine and surface fluorination of nanoparticles is the basis of the sorption in the technology of water purification from excessive fluoride. For each of these applications the understanding of changes of properties and structure of zirconia nanoparticles under fluorine influence is needed. The surface fluorination of ceramic materials may be realized by different methods but more interesting method from them is wet chemical synthesis.

In this work, we investigated the effect of fluoride surface modification on morphology, structure and surface state of yttria stabilized zirconia. Yttria stabilized zirconia nanoparticles was prepared by coprecipitation with using MW drying. The fluoride surface modification of yttria stabilized zirconia nanoparticles was carried out from NH4F solution on different syntheses stage. The concentration range of used NH4F solution was 2-20 wt. % . The fluoride was found to bind to the nanoparticles surface in a ligand exchange reaction between surface hydroxyl groups and the fluoride anions according FTIR spectroscopy data. Therefore, the influence of surface state of yttria stabilized zirconia nanopartiles, amount of fluorination agent, the surface fluorination time and annealing temperature on the properties and structure of modified systems was studied. It was shown that peculiarities of structure and surface state of zirconia nanoparticles are due to the competitive effect of yttrium ions which generate oxygen vacancies in lattice (crystal bulk) and fluoride –ions as surface-active agent.

According to DSC and FTIR data amount of fluoride ions influence on dehydratation and crystallization of zirconia and lead to change of phase composition and morphology of formed crystallic particles. The gradual transform of zirconia nanoparticles from sphere to rodlike form occurs, fig.1. The evolution of structure, surface state and morphology at transform from oxide to oxyfluoride is discussed.

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## B4.3

# MAS NMR Study of the Solidified Cryolite Systems with FeO Addition

**F. ŠIMKO** [(a)]*

[(a)] INSTITUTE OF INORGANIC CHEMISTRY, DEPT. OF MOLTEN SALTS - BRATISLAVA (SLOVAKIA)

* uachsim@savba.sk

Interaction of cryolite (Na3AlF6) with aluminium oxide plays essential role in aluminium production. It is known more than one hundred years, however, the exact reaction mechanism is still not satisfactory established. Significant part of published data deals with more or less successful proving of fluorido-oxido-aluminates (also published as oxy-fluoro or oxo-fluoro aluminates) existence. Related topic is the interaction of cryolite with other oxide compounds that are interested from Al production process aspects, like materials of inert anodes and cathodes, impurities, et al. The purpose of present work is to obtain new results by a multinuclear (27Al, 23Na and $^{19}$F) MAS NMR study of $Na_3AlF_6$−FeO binary system and explain the mechanism of dissolution of iron (II) oxide. The combination of information obtained from the observation by NMR of different nuclei enables us to discuss previously proposed model of the liquid structure, where the formation of oxo-fluoroaluminate and iron fluorinated species were confirmed (1). MAS NMR experiments of solidified samples after heating measurements with additionally prepared samples mould complex view on the reaction mechanism. MAS NMR experiments exhibit that all reaction products escape from the system at the measured temperature. Two different condensate products were acquired. High temperature one contains alumina, cryolite, chiolite and AlF3. These phases are result of relatively complicated set of processes including evaporation, condensation and decomposition. 2 $Na_3AlF_6$ (l) + 2 FeO(s) = 2 $Na_2FeF_4$(g) + $Na_2Al_2O_2F_4$(g) (A) $Na_3AlF_6$(l) = 2 $NaAlF_4$(g) + NaF(l) (B) 5$NaAlF_4$(g) = $Na_5Al_3F_{14}$ (s) + 2$AlF_3$(s) (C) 3$Na_2Al_2O_2F_4$(g) = 2$Al_2O_3$(s) + 2$Na_3AlF_6$(s) (D) Low temperature condensate contains “iron-fluorinated”paramagnetic species. (1) Šimko F., Rakhmatullin A., Boča M., Daněk V. and Bessada C., European Journal of Inorganic Chemistry (2006) 4528–4532. Acknowledgements. We would like to acknowledge the financial support of the EEC, Contract HPMC-CT-2000-00169 in the frame of the Marie Curie training site ‘high resolution solid/high temperature liquid Nuclear Magnetic Resonance in Materials sciences” (Orleans, France), and Slovak Grant Agencies (VEGA-2/0179/10, APVV-0460-10).

## B4.4

# Tetrafluorobromates for Urban Mining of Noble Metals – A Case Study on Iridium Metal

**S. IVLEV [a], P. WOIDY [b], F. KRAUS [b], V. SHAGALOV [a], I. GERIN [a], R. OSTVALD [a]**

[a] Tomsk Polytechnic University - TOMSK (RUSSIA)
[b] Technische Universität München, AG Fluorchemie - GARCHING (GERMANY)

* ivlev@tpu.ru

Scientific and industrial interest in the problem of extraction and separation of valuable components from municipal solid wastes, the so called “urban mining”, [1] is steadily growing. Such components are mainly expensive metals of lower availability, such as e.g. indium, the noble, or the rare earth metals. These are usually included in different parts of electronic devices and supplies and are present in quite low percentage. Although a lot of investigations were carried out in order to solve the problem of re-obtaining these resources, a universal solution has not been found yet.

One of the directions, where a possible solution can be developed, is simultaneous treatment of all noble metal compounds in urban solid wastes in order to turn them to complex fluorides. This method is more convenient in comparison to traditional techniques for homogenization of materials mainly due to the fact that there are no liquid wastes formed on the first stage of the process. However, a question of choosing an effective and convenient fluorinating agent arises in this case. The most obvious choice – elemental fluorine – is not always appropriate since technologies involving fluorine require special safety measures for its storage and transportation.

In this study we analyzed the possibility of using a relatively uninvestigated class of chemical compounds – the tetrafluorobromates of alkali and alkaline-earth metals [2] – for the extraction and successive separation of noble metals. Results of X-ray powder diffraction analyses of the products formed in the reactions of various tetrafluorobromates and iridium metal were obtained. Also, results of thermogravimetric and differential thermal analyses were studied to get a deeper understanding of the processes involved.

It was shown that the main product of such interaction was a corresponding metal hexafluoroiridate(IV) $Me_2IrF_6$. Besides that compound, there were found either some residual amount of metal fluorobromate(III) in case it was taken in excess, or some amount of iridium metal and a number of unidentified products in case there was lack of a fluorobromate(III).

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# STREAM C

## TUESDAY, JULY 23

## IL-C3

# Surface Structure and Wetting Behavior of Fluoroacrylate Polymers

**A. TAKAHARA** [(a)]*

[(a)] Institute for Materials Chemistry and Engineering, Kyushu University - FUKUOKA (JAPAN)

* takahara@cstf.kyushu-u.ac.jp

Polymers with fluoroalkyl ($R_f$) groups are attractive to a broad range of applications in the paint and coatings sector. The purpose of this study is to reveal the relationship between unique properties of polymers with fluoroalkyl ($R_f$) side chain groups and its molecular aggregation states.

The effect of surface molecular motion on the wetting behavior of water on the thin film surfaces of poly(fluoroalkyl methacrylate)s with various fluoroalkyl ($R_{f)}$ groups [PFMA-$C_y$; y: fluoromethylene number in $R_f$ groups, y=1, 2, 4, 6, and 8] were characterized. The receding contact angle of PFMA-$C_y$ with short $R_f$ groups (y=1, 2, 4, and 6) was larger than that of poly(fluoroalkyl acrylate) with short $R_f$ groups [PFA-$C_y$, y=1, 2, 4, and 6]. This stable hydrophobicity observed for PFMA-$C_y$ is due to the restriction of thermal molecular motion by the a-methyl group. Wide-angle X-ray diffraction (WAXD) and grazing incidence WAXD (GIWAXD) measurements revealed that the $R_f$ groups [PFMA-$C_y$, y=1, 2, 4, and 6] were not crystallized. PFMA-$C_8$ showed high advancing and receding contact angles due to the crystallization of fluoroalkyl groups at the surface region. The hydrophobicity of PFMA-$C_8$ was improved after annealing due to the ordering of fluorooctyl groups.

GIWAXD measurement of PFA-$C_8$ film revealed that the perfluorooctyl (FA8) side chain forms highly oriented bilayer lamella parallel to the surface with an absence of spherulite. A mold with a line pattern was imprinted onto a thin film of PFA-$C_8$, and the nanoimprinting(NI) characteristics of PFA-$C_8$ thin film were investigated. It was revealed that nanotexture could be imprinted on PFA-$C_8$ at room temperature because of the weak side chain interaction among the fluorooctyl groups in crystallites. The nanotextured PFA-$C_8$ film with a line pattern exhibited anisotropic wetting behavior. The anisotropic wetting behavior was attributed to the difference between the energy barriers of wetting in the direction parallel and orthogonal to the lines. The anisotropic wetting disappeared and superhydrophobicity as well as a water droplet bouncing was exhibited after the second NI.

In order to realize an environmentally friendly PFA with short FA chain. the effect of a-substituent on the molecular motion and wetting behavior of poly{2-(perfluorobutyl)ethyl acrylate} [PFA-$C_4$], poly{2-(perfluorobutyl)ethyl methacrylate} [PFMA-$C_4$], poly{2-(perfluorobutyl)ethyl a-fluoroacrylate} [PFFA-$C_4$], and poly{2-(perfluorobutyl)ethyl a-chloroacrylate} [PFClA-$C_4$] films were characterized. WAXD of oriented PFClA-$C_8$ fiber suggested the presence of rod-like chain due to the presence of bulky a-Cl group. Tg of PFFA-$C_4$ and PFClA-$C_4$ were well above the room temperature. The water repellencies of PFFA-$C_4$ and PFClA-$C_4$ were as high as that of PFMA-$C_4$ and their oil repellency of PFFA-$C_4$ and PFClA-$C_4$ was higher than the PFMA-$C_{4.}$ This result was originated from the low main chain mobility of PFFA-$C_4$ and PFClA-$C_4$ due to the presence of bulky a-substituents. The effect of molecular mobility on water repellency was clarified by the results of temperature dependent studies of dynamic contact angle, LFM, and the surface chemical composition measured by XPS.

## C3.1

# Superhydrophobic fluorinated surfaces and comparison with their hydrocarbon analogues

**M. WOLFS** [(a)]*, **T. DARMANIN** [(a)], **F. GUITTARD** [(a)]*

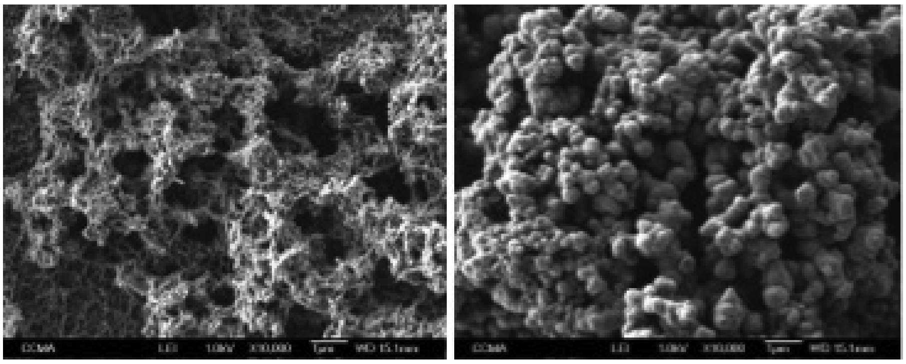
[(a)] Univ. Nice Sophia Antipolis, CNRS, LPMC, UMR7336, Parc Valrose - NICE (FRANCE)

* guittard@unice.fr

melanie.wolfs@unice.fr

Research on superhydrophobic surfaces (i.e. surfaces with a water contact angle larger than 150° and low hysteresis and sliding angle) has exponentially grown for the last decade because of the interest in both scientific and industrial communities. Superhydrophobicity results from the combination of low surface energy materials with an appropriate surface structuration. In nature, many biological materials exhibit water-repellency properties. These surfaces inspired scientists to develop various biomimetic and bioinspired approaches to build materials with superhydrophobic properties.

Electropolymerization is a fast, reproducible and versatile method to make superhydrophobic surfaces. Morphology and surface growth are governed not only by the monomer chemical structure (polymerizable core, substituent)[1-3] but also by the electrochemical parameters (deposition charge, solvent, doping agent, electropolymerization technique,…).[2] This work presents some examples of fluorinated superhydrophobic polymer surfaces made by electrochemical polymerization and the comparison of their anti-wetting properties with hydrocarbon analogues. Water repellency could be obtained with bioinspired hydrocarbon conducting polymers. This work contributed to the elaboration of bioinspired surfaces with an ecotoxic-friendly approach.



*SEM images of Fluorinated and Hydrocarbon derivatives polymer surfaces (magnification x 10 000).*

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## C3.2

# Efficient Mineralization of Fluorinated Ionic Liquid Anions Using Subcritical and Supercritical Water

**H. HORI** [(a)]*, **A. TAKAHASHI** [(a)], **Y. NODA** [(a)], **T. SAKAMOTO** [(a)]
[(a)] KANAGAWA UNIVERSITY, FACULTY OF SCIENCE - HIRATSUKA (JAPAN)
* h-hori@kanagawa-u.ac.jp

Ionic liquids (ILs) have been widely studied for green chemistry applications. Especially, fluorinated ILs, that is, ILs bearing perfluorinated organic anions, are being used in many electrochemical devices such as lithium-ion batteries, polymer electrolyte membrane fuel cells and so forth, owing to their specific characters such as non-flammability, high thermal stability, wide electrochemical windows, and high ion conductivity. For their wider use, waste treatment techniques will have to be established for them. If they could be decomposed to $F^-$ ions by means of environmentally benign techniques, the well-established protocol for the treatment of $F^-$ ions could be used: $Ca^{2+}$ is added to the system to form $CaF_2$, which is a raw material for hydrofluoric acid. Thus, the development of such techniques would allow for the recycling of a fluorine resource, the global demand for which is increasing.

We previously demonstrated that fluorochemical surfactants such as bioaccumulative perfluorooctanesulfonate (PFOS) [1] and PFOS alternatives [2] are efficiently decomposed in subcritical water in the presence of a metal such as iron,and the methodology was successfully applied to the decomposition of a perfluorinated ion-exchange membrane [3].

Herein we report on the decomposition of typical fluorinated IL anions, bis(perfluoroalkanesulfonyl)imide anions $[(CF_3SO_2)_2N]^-$ and $[(C_4F_9SO_2)_2N]^-$, in subcritical and supercritical water, in the presence of an oxidizing agent ($O_2$) or reducing agents (Fe, FeO). An effective methodology for the decomposition of the fluorinated chemicals is presented.

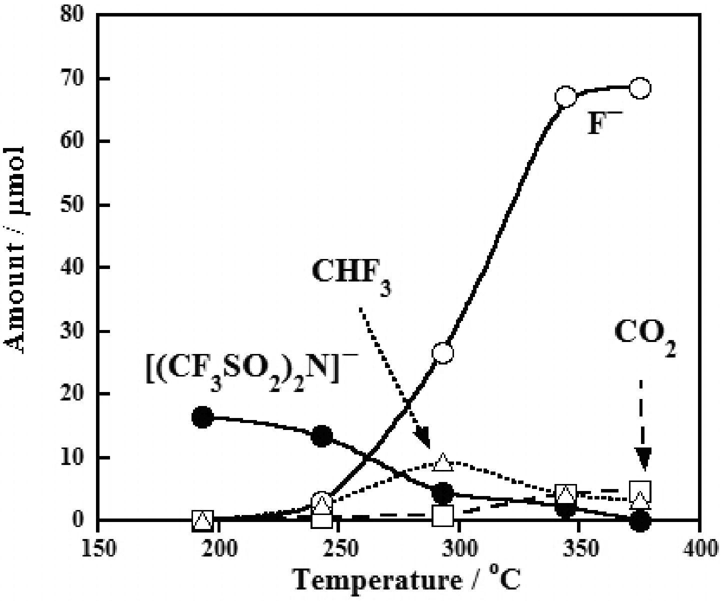

*Fig. 1. Temperature dependence of the decomposition of* $([CF_3SO_2)_2N]^-$ *in the presence of iron.*

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## C3.3

# Porous materials templated by fluorinated surfactant-based systems

**J. BLIN** [(a)]*, **M.J. STEBE** [(a)]

[(a)] Structure et Réactivité des Systèmes Moléculaires Complexes - VANDOEUVRE LES NANCY (FRANCE)

* Jean-Luc.Blin@univ-lorraine.fr

This work deals with the study of the properties of nonionic fluorinated surfactant based systems which are related to the synthesis of porous silica. In particular we have investigated the effect of the incorporation of additive on the mesopores ordering. Ordered mesoporous materials can be prepared according to the self assembly mechanism by using micelles as building blocks. However we have shown that the mesopore ordering is related to the position of the cloud point curve. The ordered mesoporous materials can also be obtained by using fluorinated liquid crystals phase as fingerprint through the liquid crystal templating process. In this case there is a correlation between the hydrophobic diameters of the rods of the $H_1$ phase and the mesopore diameters of the silica materials. The solubilization of fluorocarbons in the fluorinated micelles can lead to microemulsions, which gives rise to large pore mesoporous materials. Thus, the mesopore size can be tailored by adding fluorinated oils as swelling agents. The further addition of the fluorocarbons into the systems can involve the formation of emulsions, which can be used as template for the design of hierarchical porous materials. However we have shown that the synthesis of these hierarchical materials is related to the phase inversion temperature of the system.

## IL-C4

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# Fluoropolyether elastomers having low glass transition temperatures

**S. CORVELEYN (a), G. MIKE (b), W. GROOTAERT (c), T. OPSTAL (a), G. DAHLKE (c), R. DAMS (a)***

(a) 3M BELGIUM, MATERIAL RESOURCE DIVISION -R&D - ZWIJNDRECHT (BELGIUM)
(b) 3M USA ,CRML - ST PAUL (USA)
(c) 3M USA , AdMD, Dyneon R&D - ST PAUL (USA)

* rdams1@mmm.com

Fluoroelastomers are widely used in the industry - for example the automotive or chemical industry - because they retain their elastomeric properties over a wide temperature range and have high resistance to heat , chemicals and fuels . In many applications , for example in aircraft or aerospace , it is desirable that the fluoropolymers keep their elastomeric properties at very low temperatures , for example below -40°C for an extended period of time . In this communication , an overview will be given on curable compositions for making fluoroelastomers having a glass transition temperature below -50°C . Triazine and peroxide cured systems will be discussed .

## C4.1

# Suspension polymerization kinetics of TFE

**P. CROUSE [(a)]*, M. MABUDAFHASI [(a)], T. KILI [(a)], J. VAN DER WALT [(b)], C. THOMPSON [(b)]**
[(a)] UNIVERSITY OF PRETORIA - PRETORIA (SOUTH AFRICA)
[(b)] NECSA - PRETORIA (SOUTH AFRICA)
* philip.crouse@up.ac.za

Despite the large range of commercial fluoropolymers now available, PTFE still forms the bulk of the market, seventy-five years after its discovery. Furthermore, despite the fact that the polymer has been in the market for such along period, surprisingly few quantitative results regarding the kinetics of its formation have been published. Undoubtedly these are available within the research facilities of the large production companies, but evidently not in the public domain. The free-radical suspension polymerization kinetics is reported here, extracted from data generated in a 300 mL reactor vessel. Ammonium bisulphate was used as initiator. The monomer was fed into the reactor in the gas phase, being supplied at constant pressure by maintaining the condensed liquid monomer at constant temperature. Adequate agitation ensured that we could work in a regime where mass transfer was not rate limiting. Initiator feed rate and temperature were the input variables for this study. TFE flow was monitored using a Coriolis mass flow meter. The experimental data are fitted to a slightly-modified classic initiation-propagation-termination model [*e.g.* 1,2], yielding Arrhenius expressions adequate for scaling. Particle agglomeration and growth complicates extraction of exact data.

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## C4.2

# Synthesis of Novel Perfluorinated Sulfonyl Azides and partially Fluorinated Alkyl Azides as new Crosslinking Agents for Fluoropolymers

**I. WLASSICS** [(a)*], **A. MARRANI** [(a)], **V. TORTELLI** [(a)], **I. FALCO** [(a)]

[(a)] SOLVAY SPECIALTY POLYMERS ITALY SPA, NEW FLUORINATED MATERIALS - MILANO (ITALY)

* ivan.wlassics@solvay.com

A fundamental step in the synthesis of any polymer, including therefore Fluoropolymers, is the final cross-linking, or vulcanization. With respect to the cross-linking reaction, azides, $RN_3$, are a particularly attractive class of compounds due to their ease of synthesis, high reactivity in relatively mild reaction conditions, generate inert, and easily removable reaction side products ($N_2$).

In this presentation, a series of novel per-fluorinated allyl-ether or vinyl-ether sulfonyl azides, partially fluorinated vinyl alkyl azide monomers and partially fluorinated alkyl diazides were synthesized and used either as cross-linking agents or as cure-site monomers for the ferro, piezo and pyroelectric polymer, a Trifluoroethylene/Vinylidene fluoride (TrFE/VDF – 25/75 in moles) co-polymer [1, 2, 3].

The di-azides or azide containing co-polymer were then activated either thermally (130°C) or by U.V. irradiation yielding the corresponding alkyl or sulfonyl nitrenes which in turn may react with $–CH_n-$ groups by way of an insertion reaction [4], with olefins yielding triazolines which in turn yield the corresponding aziridines following thermal or UV irradiation [5], with another nitrene yielding the corresponding diazo compound[6]. Some experimental evidence may even indicates that sulfonyl azides also decompose yielding a stable C-C bond cross-link.

The syntheses of the new azidic monomers, possible crosslinking mechanisms, crosslinking evidence of P(VDF-TrFE) copolymers, performance of azide cross-linked P(VDF-TrFE) copolymers will be presented and discussed.

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## C4.3

# Synthesis of Fluorine-containing Water-Soluble Polymers and Study of Their Temperature-Responsive Behaviours

**T. IRITA** [(a)]*, **T. NAGAI** [(a)], **K. ADACHI** [(a)], **S. KANAOKA** [(b)], **S. AOSHIMA** [(b)]
[(a)] DAIKIN INDUSTRIES, LTD., CHEMICAL R&D CENTRE - OSAKA (JAPAN)
[(b)] Department of Macromolecular Science, Osaka University - OSAKA (JAPAN)
* tomomi.irita@daikin.co.jp

Well-defined water-soluble fluorinated polymers (WFP) with oxyethylene units and different fluorinecontent were successfully prepared by living cationic polymerization. Poly(vinyl ether)s with oxyethylene units is known to be a thermo-responsive polymer, exhibits a lower critical solution temperature (LCST) in aqueous solution. Recently, we have constructed various types of thermosensitive self-assembling systems in aqueous solutions using poly(vinyl ether)s with oxyethylene units in the presence of a weak Lewis base[1-2]. Temperature-responsive behaviour was largely affected by the primary structures of polymers. Although the precision synthesis of poly(N-isopropylacrylamide) allowed independent similar studies quite recently, there were still few examples of detailed investigations on the effect of hydrophobic groups on LCST-type thermosensitive phase separation. The unique incompatibility of fluoroalkyl groups would be a great advantage for realizing temperature responsive phase separation of a polymer-solvent system, such as LCST-type transition in aqueous solution. Since vinyl ether polymers with oxyethylene chains usually exhibit good solubility to water, sensitive thermoresponsive phase separation in aqueous solution was expected with a polymer consisting of such a vinyl ether skeleton and fluorinated pendant groups due to their hydrophobic/ hydrophilic balance.

In this paper, we describe the precision synthesis of series fluorine-containing poly(vinyl ether)s via living cationic polymerization, and discuss the relationship between polymer shapes and their thermosensitive behaviour. These new fluorine-containing polymers with oxyethylene were therefore also thermo-responsive and demonstrate good water-soluble. Significant differences in the cloud points were observed with shorter endfunctionalized polymers. In addition, a polymer having no fluorine group showed no cloud point below at least 60 ºC in aqueous solution. After the fluorine functions were initiated into terminal groups, the cloud point of this polymer was decreased almost 20 ºC in aqueous solution. The enhanced solubility of the star polymer is attributed to the ionized carboxy groups covering the surface of the star molecule.

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## C4.4

# Surface treatment on polymer packaging films using various fluorination routes

**J. PEYROUX** [(a)]*, **M. DUBOIS** [(b)], **E. TOMASELLA** [(b)], **A.P. KHARITONOV** [(c)], **D. FLAHAUT** [(d)]

[(a)] Institut de Chimie de Clermont-Ferrand, MATERIAUX INORGANIQUES - AUBIERE CEDEX (FRANCE)
[(b)] Institut de Chimie de Clermont-Ferrand - AUBIERE CEDEX (FRANCE)
[(c)] Institute of Energy Problems of Chemical Physics (Branch) of the Russian Academy of Sciences - CHERNOGOLOVKA (RUSSIA)
[(d)] Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux/Equipe Chimie-Physique - PAU CEDEX (FRANCE)

* jeremy.peyroux@univ-bpclermont.fr

Commonly used polymer packaging films display not only many advantages, such as low cost and processability but exhibit also few drawbacks such as poor adhesion, printability, low barrier properties and chemical resistance. Moreover, it is also possible to obtain the whole articles from specials polymers or starting from multilayers packaging films but these kinds of process remain restricted due to the high cost and high complexity of synthesis. The present work focuses on the modification of their surface properties by **different fluorination routes**.

Indeed, fluorination is well known to improve polymers surface properties. It is a diffusion-controlled process which may be defined as a heterogeneous reaction between a gas (pure molecular fluorine $F_2$ or mixed with an inert gas) with the polymer surface mainly at room temperature. This method modifies only the upper surface layer. Concerning the bulk properties, they remain unchanged. This process, recognized as a safe and dry technology, occurs a lot of advantages which allows it to be used for industrial applications.

Different fluorination conditions were investigated with various commercial polymers using two different fluorinating agents: **pure molecular fluorine ($F_2$) and atomic fluorine ($F^·$).** Atomic fluorine ($F^·$) was generated by the decomposition of solid or gaseous fluorinating reactants. Examples with $XeF_2$ (g) will be given. It was decomposed thermally in contact with the target defined to fluorinate in Xe (g) and $2F^·$.

Modifications of the surface layer have been characterized using various complementary techniques such as Fourier Transform Infrared (FT-IR) spectroscopy (ATR and transmission modes), high resolution solid state Nuclear Magnetic Resonance (NMR) ($^{19}F$) which are suitable to determine the nature of the C-F bonding and the fluorinated groups (CF, CHF, $CF_2$, $CF_3$). X-ray Photoelectron Spectroscopy (XPS) was also performed to extract the surface chemical compositions according to the thickness.

The main objective is to understand the different reactivity, diffusion processes leading to different mechanisms of fluorination between these two processes. The resulting properties were then studied showing that the synthetized fluorinated layer reduces the friction coefficient and improves chemical resistance. To support our study, measurements of surface energy have been also realized underlining the enhancement of the adhesion properties and the change of hydrophobic/hydrophilic character.

# MOISSAN SESSION

## TUESDAY, JULY 23

## IL-M1

# Chemical Synthesis of Elemental Fluorine

**K. CHRISTE** [(a)]*

[(a)] LOKER RESEARCH INSTITUTE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA - LOS ANGELES (USA)

* kchriste@usc.edu

The first documented and unsuccessful attempts to prepare elemental fluorine by purely chemical methods date back to 1811 by Davy who at the suggestion of Ampere also proposed the name fluorine for the still unknown element. Although elemental fluorine can occur in nature trapped in fluorites containing other radioactive minerals and was first detected by its smell in crushed Woelsendorf Stinkspat by Hoffmann in 1816, its identification as fluorine remained controversial until Moissan prepared in 1886 large amounts of it electrochemically. He also concluded in 1891 that the related mineral antonozite contained some elemental fluorine. In spite of this, the occurrence of free $F_2$ in certain fluorite minerals remained uncertain until 2012, when Kraus and coworkers demonstrated its occurrence in the Woelsendorf Stinkspat by magic angle spinning $^{19}F$ NMR spectroscopy. Both of the above formation methods of elemental fluorine require external energy sources, such as electrolysis or β-irradiation, and all efforts, including those by Davy, Faraday, Fremy, Moissan, and Ruff, to prepare $F_2$ by purely chemical means had failed. As a consequence, every major inorganic textbook prior to 1986 stated that it was impossible to prepare elemental fluorine by chemical means because fluorine is the most electronegative element and therefore cannot be displaced from its compounds by another element. This dogma was destroyed by Christe in 1986 at the 100th jubilee of the discovery of fluorine by Moissan. Details leading to this historic discovery will be presented.

## IL-M2

# My Favorite Molecules

**D. DESMARTEAU** [(a)]*

(a) CLEMSON UNIVERSITY, Department of Chemistry - ANDERSON (USA)

* fluorin@clemson.edu

Fifty years in fluorine chemistry have given me the opportuity to carryout reseaerch in many different areas. For me the excitement has always been the discovery of new compounds and materials and the often unanticipated directions thse discoveries have taken me and my coworkers. In this brief lecture, I want to illustrate this using two early discoveries in our research. One involves the first example of a xenon-nitrgen bond in $FXeN(SO_2F)_2$ and the other a simple peroxide $CF_3OOH$. Appropriately, both of these were possible due to Moisan's isolation of elemental fluorine.

## IL-M3

# The importance of fluorine in catalysis with organometallic fluorides and in compounds with low valent main group elements

**H.W. ROESKY** [(a)]*

[(a)] UNIVERSITY OF GÖTTINGEN, Instiitute of Inorganic Chemistry - GÖTTINGEN (GERMANY)

* hroesky@gwdg.de

Compounds of organometallic fluorides in catalysis are hardly known. This has two reasons. On the one hand the metal-fluorine bond is stronger when compared with all the other metal halide bonds, and therefore they seem not to be reactive enough. On the other hand soluble organometallic fluorides are not easy to prepare. They easily disproportionate or dismutate. Therefore we developed special organometallic tin(IV)- and organometallic tin(II) fluorides as fluorinating agents.

The catalysis of organotitanium fluorides in the polymerization of styrene will be demonstrated.

The preparation of LSn(:)F with a two valent tin atom will be reported and its application in the preparation of fluorine containing stable biradicals will be shown. The driving motivation for low valent silicon is the present high energy converting process for preparing silicon of high oxidation states.

## IL-M4

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# Synthesis and physical chemical properties of inorganic fluorides: «From single crystals to functionalized nanofluorides»

**A. TRESSAUD** [(a)]*

[(a)] ICMCB-CNRS, Université Bordeaux 1 - PESSAC (FRANCE)

* tressaud@icmcb-bordeaux.cnrs.fr

The outstanding oxidizing properties of fluorine gas and fluorinated media, combined with most appropriate characterization techniques have allowed to isolate fluorinated and oxyfluorinated series with unique physical chemical properties. These properties can be efficaciously modulated by inducing structural modifications in the networks.

By properly choosing the synthesis route, inorganic solid fluorides and oxyfluorides can be prepared either as single crystals, bulky materials [1], thin layers, or highly divided nanostructured products [2]. Surface treatments by exposure to reactive fluorinated atmospheres can be alternatively used for modifying and functionalizing, even at room temperature, the surface of various materials such as polymers, metals, biomaterials, carbon-based compounds, inorganic ceramics and powders [3].

The wide range of salient physical chemical properties and peculiarities of these fluoro-compounds can be illustrated by various examples, including ferri- and ferromagnetism in perovskite-derived compounds, piezoconductivity in $M^{II}M^{IV}F_6$ fluorides [4], ferroelasticity in elpasolites and pyrochlore-derived phases [5], high $T_c$ superconductivity, surface functionalization of various materials: alumina-, silica- and carbon-based substrates [6], salient optical properties, potential applications in catalysis and energy storage [7].

The relationships between structural networks, morphological features and physical chemical properties will be emphasized.

Those who helped and supported me during these last decades should be acknowledged: A. Demourgues, E. Durand, C. Labrugère, M. Gaudon, J. Majimel, permanent members of the ICMCB Group // D. Dambournet, L. Francke, D. Pauwels, N. Penin, H. Serier, E. Lataste, R. Clarenc, C. Pepin, PhD students // J. Grannec, L. Lozano, L. Fournès, J. Darriet, B. Chevalier, J.P. Chaminade, J.M. Dance†, previous colleagues of LCS (from 1964), then ICMCB. In addition, fruitful cooperative programs with foreign labs worldwide should not be forgotten, in particular with groups of D. Babel (Germany), J.P. Issi (Belgium), P. Nuñez (Spain), B. Zemva (Slovenia), I. Flerov (Russia), T. Nakajima & H. Touhara (Japan), M. Leblanc & H. Groult (France).

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# WEDNESDAY, JULY 24

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## Morning 9:00 – 10:30

## STREAM A

CHAIR: V. GOUVERNEUR, ***Oxford University, Oxford*** *(UK)*

**9:00** **IL-A5** Invited Lecture
APPLICATIONS OF PET IN MEDICAL IMAGING
**A. Luxen**
*Université de Liège, Centre de Recherche du Cyclotron, Liège (Belgium)*

**9:30** **A5.1** THE FLUORINASE ENZYME APPLIED TO PEPTIDE $^{18}$F-LABELLING FOR POSITRON EMISSION TOMOGRAPHY (PET)
**D. O'Hagan**
*University of St Andrews, Biomolecular Sciences, Research Complex, St Andrews (UK)*

**9:50** **A5.2** ACCESS TO WATER SOLUBLE SULFONATED $^{18}$F-LABELLED COMPOUNDS BY SULFONE OPENING WITH [$^{18}$F]FLUORIDE: AN EFFICIENT $^{18}$F-LABELLING STRATEGY FOR PET IMAGING
S. Schmitt, L. Barre, **C. Perrio**
*CNRS-CEA-UCBN, LDM-TEP, UMR6301 ISTCT, CYCERON, Caen (France)*

**10:10** **A5.3** SYNTHESIS OF FLUORINE-18 RADIOLABELED 5-HT$_6$ LIGANDS FOR PET IMAGING
**J. Colomb**, G. Becker, D. Le Bars, L. Zimmer, T. Billard
*Université Lyon1, ICBMS (France)*

## STREAM B

CHAIR: E. ANTIPOV, ***Moscow State University, Moscow (Russia)***

**9:00** **IL-B5** Invited Lecture
FLUOROCARBON ORGANIC ACCEPTORS: FUNDAMENTALS AND APPLICATIONS
**O. Boltalina**, S.H. Strauss, I. V. Kuvychko, K. P. Castro, L. K. Sun, T. T. Clikeman, B. W. Larson, J. B. Whitaker, S. N. Spisak, A. A. Popov, M. A. Petrukhina, S. H. M. Deng, X. B. Wang
*Colorado State University, Dept of Chemistry, Fort Collins (USA)*

**9:30** **B5.1** **GRAPHITE INTERCALATION COMPOUNDS AND IONIC LIQUID CRYSTALS BASED ON $(AlF_4)^-$ AND MOLECULAR GEOMETRY OF $(Al_2F_9)^{3-}$**
**K. Matsumoto**, K. Takagi, F. Xu, R. Hagiwara
*Kyoto University, Graduate School of Energy Science , Kyoto (Japan)*

**9:50** **B5.2** **A NEW GENERATION OF HYBRID CARBON-FLUOROCARBON NANOCOMPOSITE MATERIALS FOR ELECTROPHYSICAL AND ELECTROCHEMICAL APPLICATIONS**
**V. N. Mitkin**
*Nikolaev Institute of Inorganic Chemistry, SB RAS, Laboratory of Carbon Materials Chemistry, Novosibirsk (Russia)*

**10:10** **B5.3** **FLUORINE MEETS BUCKYBOWLS**
B. M. Schmidt, B. Duda, B. Topolinski, S. Seki, H. Sakurai, **D. Lentz**
*Freie Universität Berlin, Institut für Chemie und Biochemie, Berlin (Germany)*

## STREAM C

CHAIR: **I. WLASSICS**, *Solvay Specialty Polymers Italy Spa (Italy)*

**9:00** **IL-C5** **Invited Lecture**
**INNOVATIVE METHODOLOGY FOR THE PREPARATION OF QUATERNARY AMMONIUM PERFLUOROALKOXIDES**
**C. M. Friesen**, B. J. Jelier, J. L. Howell
*Trinity Western University, Dept of Chemistry, Langley, BC (Canada)*

**9:30** **C5.1** **VERSATILITY IN THE FUNCTIONAL PROPERTIES OF FLUOROUS TRIAZOLES AND TETRAZOLES**
D. V. Francis, J. B. Harper, A. I. Mohammed, **R. W. Read**
*University of New South Wales, School of Chemistry, Sydney (Australia)*

**9:50** **C5.2** **PERFLUORO-TAGGED METAL NANOPARTICLES SUPPORTED ON SILICA-GEL AS HIGHLY ACTIVE RECOVERABLE CATALYSTS**
**A. Vallribera**
*Universitat Autonoma de Barcelona, Dept Chemistry, Barcelona (Spain)*

**10:10** **C5.3** **FLUORINATED SULFOXIMINES AS POTENTIAL LIGANDS FOR CATALYSIS**
**P. Diter,** T.N. Le, E. Magnier, B. Pegot, M. Toffano, C. Bournaud, G. Vo-Thanh
*Université de Versailles-Saint Quentin-CNRS, Equipe Fluor (France)*

**10:30 – 11:00** *Coffee*

# Morning 11:00 – 12:30

## STREAM A

**CHAIR:** **Y. YAGUPOLSKII, *Institute of Organic Chemistry, Kiev (Ukraine)***

**11:00** **IL-A6** **Invited Lecture**
**SYNTHESIS & REACTION OF SOME FLUORINE-CONTAINING PHOSPHONIUM SALTS**
**J.-C. Xiao,** J. Zheng, J. Cai
*Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, Shanghai (China)*

**11:30** **A6.1** **FLUOROALKENES SYNTHESIS FROM BENZOTHIAZOLYL DERIVATIVES**
**F. Larnaud**, E. Pfund, B. Linclau, T. Lequeux
*ENSI Caen & Université de Caen, LCMT (France)*

**11:50** **A6.2** **SYNTHETIC APPLICATION OF ß-(TRIFLUOROMETHYL)VINYL SULFONIUM SALT**
**T. Hanamoto,** R. Maeda, R. Ishibashi, N. Kasai, Y. Takehiro, H. Furuno
*Saga University, Dept of Chemistry & Applied Chemistry, Saga (Japan)*

**12:10** **A6.3** **SYNTHESIS OF FLUORINATED BUILDING BLOCKS BY [3,3]-SIGMATROPIC REARRANGEMENTS**
**G. Haufe**, A. L. Dreier, D. Ramb, J. S. Thrasher
*Universität Münster, Organisch-Chemisches Institut, Münster (Germany)*

## STREAM B

**CHAIR:** **M. LEBLANC, *Le Mans University, Le Mans (France)***

**11:00** **IL-B6** **Invited Lecture**
**MAGNETIC FRUSTRATION IN VANADIUM FLUORIDE-BASED KAGOME LATTICES**
**P. Lightfoot**
*University of St Andrews, School of Chemistry, St Andrews (UK)*

**11:30** **B6.1** **FLUORIDE-BASED MODULES FOR MOLECULAR MAGNETIC MATERIALS**
**K. Pedersen**, J. Bendix, R. Clérac
*University of Copenhagen, Dept of Chemistry, Copenhagen (Denmark)*

**11:50** **B6.2** **UNUSUALLY STRONG ANTIFERROMAGNETIC SUPEREXCHANGE COUPLING IN PEROVSKITE KAgF$_3$**
D. Kurzydlowski, Z. Mazej, Z. Jaglicic, Y. Filinchuk, **W. Grochala**
*Warsaw University, CENT and Fac. Chem., Warsaw (Poland)*

**12:10** **B6.3** **ION MOBILITY AND TRANSPORT PROPERTIES OF SOLID SOLUTIONS IN THE PbF$_2$–Na(Rb)F–BiF$_3$. SYSTEMS ACCORDING TO NMR AND CONDUCTIVITY DATA**
V. Kavun, **V. Kharchenko**, V. Goncharuk, I. Telin, N. Uvarov
*Institute of Chemistry, Feb RAS, Laboratory of ESQCS, Vladivostok (Russia)*

## STREAM FMEC

**CHAIR:** **T. GOTO, *Doshisha University, Kyotonabe (Japan)***

**11:00** **IL-FMEC6** **Invited Lecture**
**THE CHEMISTRY OF MOLTEN SALT REACTOR FUEL**
**R. Konings**, O. Beneš
*European Commission, Institute for Transuranium Elements, Karlsruhe (Germany)*

**11:30** **FMEC6.1** **CLASSIFICATION OF SEVERAL FLUORIDE MOLTEN SALTS ACCORDING TO THEIR FLUORO-ACIDITY PROPERTIES**
**S. Delpech**, S. Jaskierowicz, D. Rodrigues
*CNRS, IPN Radiochimie, Orsay (France)*

**11:50** **FMEC6.2** **THERMODYNAMIC CONTRIBUTION TO THE STUDY OF FLUORIDE COMPOUNDS FOR FRONT END NUCLEAR CYCLE**
**S. Chatain**, J. Flèche, B. Morel, C. Gueneau
*CEA, DPC/SCCME/LM2T, Gif-Sur-Yvette (France)*

**12:10** **FMEC6.3** **INVESTIGATION OF MOLTEN FLUORIDE SYSTEMS CONTAINING NIOBIUM BY ELECTROCHEMICAL AND CARBOTHERMAL REDUCTION METHODS**
**S. Kuznetsov**
*Institute of Chemistry, Kola Science Centre RAS, High Temperature Chemistry & Electrochemistry, Apatity (Russia)*

**12:30 – 13:30** *Lunch*

**13:30 – 15:30** **POSTER SESSION (COFFEE AVAILABLE)**

**16:00 – 18:30** **CRUISE ON SEINE RIVER**

**RECEPTION“ PARIS V$^{TH}$ DISTRICT - CITY HALL”**

**19:00 – 21:00** **PRESENTATION OF “AWARD OF BEST POSTER ON SUSTAINABILITY” SPONSORED BY SOLVAY SPECIALTY POLYMERS**

# STREAM A

## WEDNESDAY, JULY 24

## IL-A5

# Applications of PET in medical imaging

**A. LUXEN** (a)*

(a) Université de Liège, Centre de Recherches du Cyclotron - LIEGE (BELGIUM)

* aluxen@ulg.ac.be

Imaging techniques such as magnetic resonance imaging (MRI), functional magnetic resonance imaging (fMRI), computed tomography (CT), single photon emission computed tomography (SPECT) and positron emission tomography (PET) have become important tools in clinical routine. All techniques have unique applications, with advantages and limitations.

Positron emission tomography (PET) allows noninvasive visualizationand quantitative assessment of physiologic and biochemical processeswithin the human body. Most of the radiopharmaceuticals used routinely in clinics are labeled with F-18.

This talk will explore three major topics: a) Recent advances in the F-18 labeling of target specific agents and drug candidates; b) GMP production of the radiopharmaceuticals; c) Recent medical applications in neurology and oncology.

## A5.1

# The fluorinase enzyme applied to peptide $^{18}$F-labelling for positron emission tomography (PET)

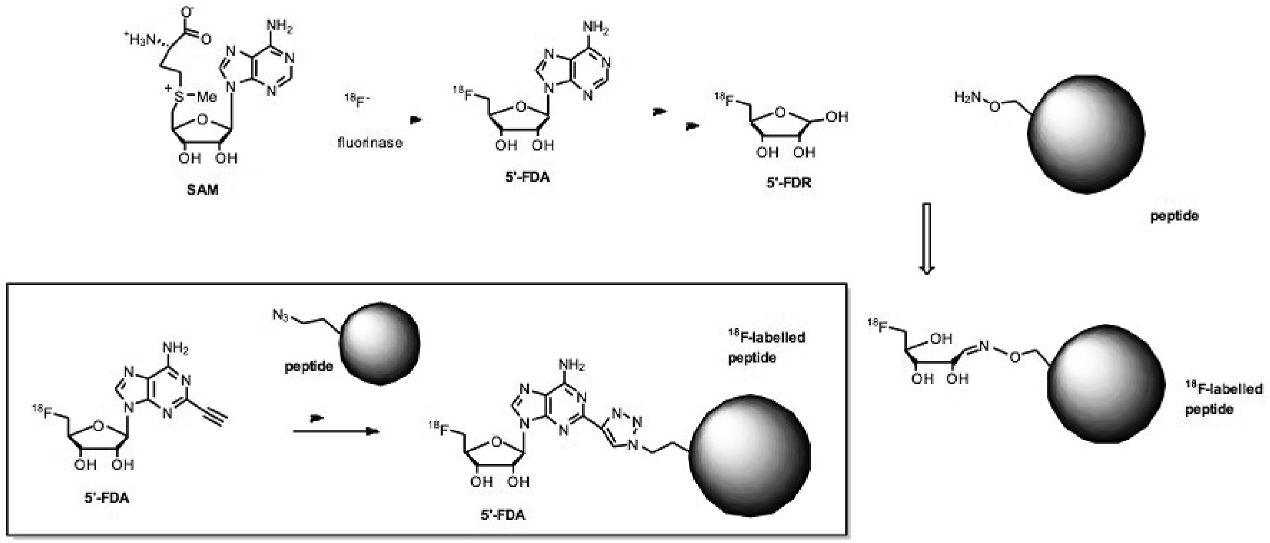
**D. O'HAGAN** [(a)]*

[(a)] Biomolecular Sciences Research Complex, University of St Andrews - ST ANDREWS (UNITED KINGDOM)

* do1@st-andrews.ac.uk

Although organo fluorine natural products are extremely rare, *Streptomyces cattleya* has the unusual capacity to biosynthesise organo-fluorine molecules. The fluorination enzyme has been identified and isolated from the organism. The *fluorinase* has been shown to mediate a reaction between S-adenosyl-L-methionine (SAM) and fluoride ion to generate 5’-fluoro-5’-deoxyadenosine (5’-FDA). The enzyme has been cloned, over-expressed and crystallised.[1]

In particular applications using the fluorinase for positron emission tomography (PET) will be highlighted, whereby the enzyme can be used to incorporate the $^{18}$F isotope from $^{18}$F$^-$fluoride ion to generate [$^{18}$F] compounds for bioconjugation to peptides.[3]



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## A5.2

# Access to water soluble sulfonated $^{18}$F-labelled compounds by sultone opening with [$^{18}$F]fluoride: an efficient $^{18}$F-labelling strategy for PET imaging

**S. SCHMITT** [(a)], **L. BARRE** [(a)], **C. PERRIO** [(a)]*

[(a)] LDM-TEP, UMR6301 ISTCT, Cyceron, CNRS-CEA-UCBN - CAEN (FRANCE)

* perrio@cyceron.fr

Objectives. Incorporation of fluorine-18 into biopolymers (i.e. peptides, proteins, oligonucleotides or antibodies) that are becoming more widely used as in vivo imaging agents, remains problematic [1]. Despite recent advances in direct method by formation of $^{18}$F-Si, $^{18}$F-B or $^{18}$F-Al bonds, current labelling strategies involve multistep approaches that include introduction of readily prepared [$^{18}$F]F- into small organic prosthetic groups, their activation and subsequent coupling to specific functional groups within the macromolecule. Although a limited number of chemical reactions have been utilized to incorporate the prosthetic groups into biopolymers [mainly acylation, alkylation, oxime or hydrazine formation, and Huisgen 1,3-dipolar cycloaddition (click chemistry)], a variety of $^{18}$F-labelled prosthetic groups have been reported. The latter usually are of lipophilic nature that has been proved to lead to increased hepatobiliary excretion. As an alternative, hydrophilic prosthetic groups were considered highly desirable. We set out to develop a platform technology based on the sultone opening with [$^{18}$F]fluoride anion which would allow the production of water soluble sulfonated $^{18}$F-labelled compounds [2]. Access to $^{18}$F-labelled biopolymers by our chosen method was achieved starting from appropriately functionalized sultones according a two-step procedure including radiofluorination then ligation to the target vector. The apolar sultone/polar sulfonic derivatives conversion was advantageous in terms of the purification of the radiofluorinated sulfonic acid derivatives, whilst facilitating automation of the process.

Results and conclusion. Sultones were converted to the corresponding [$^{18}$F]fluorosulfonates in 15-80% radiochemical yields. The optimum radiochemical yields were obtained from propane sultones after 5 min reaction time. SPE purification led to [$^{18}$F]fluorosulfonates with high chemical purities. Only traces of the sultone precursors (10 mg, <50 nmol) were remained. Ligation to various vectors was achieved in 20-60% radiochemical yields.

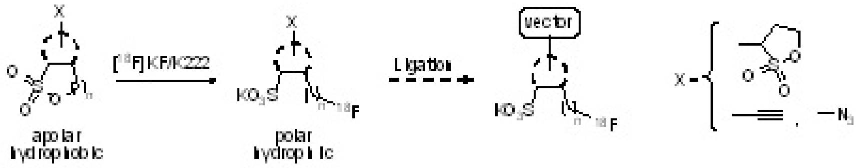

Fig. 1. Radiolabelling with fluorine-18 of vectors via radiofluorination of sultones.

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[2] S. Schmitt et al, *Chem Commun* **47** (2011), 11465.

## A5.3

# Synthesis of fluorine-18 radiolabeled 5-$HT_6$ ligands for PET imaging

**J. COLOMB [(a)], G. BECKER [(b)], D. LE BARS [(b)], L. ZIMMER [(c)], T. BILLARD [(a)*]**

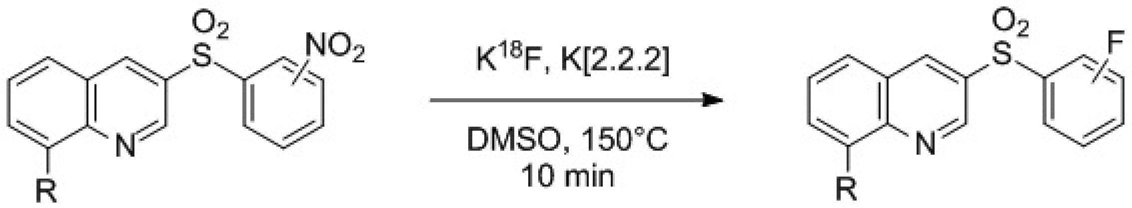
[(a)] UNIVERSITÉ CLAUDE BERNARD - LYON 1, ICBMS (UMR CNRS 5246) - LABORATOIRE SURCOOF - VILLEURBANNE (FRANCE)
[(b)] CERMEP - BRON (FRANCE)
[(c)] CRNL - BRON (FRANCE)

* thierry.billard@univ-lyon1.fr

5-$HT_6$ serotonin receptor has been recently discovered and it is distributed almost exclusively in the central nervous system (CNS) and has effect on neurodegenerative disease such as Alzheimer disease. In-vivo studies by bioimaging technique will be interesting to identify the physiological effect of this receptor and to develop a diagnostic method and to facilitate the development of potential treatment.

Development of specific 5-$HT_6$ radioligands labeled with fluorine 18 that could be used in positron emission tomography (PET), a non-invasive medical imaging technique. Those new ligands will require some parameters to target exclusively the CNS (particularly to get through the blood brain barrier) and to be easily radiolabeled with fluorine 18 in the last steps of the synthesis, due to the short half-life of fluorine 18. The synthesis of radioligands was inspired by the 5-$HT_6$ pharmacophore, recently described. Their radiolabeling give good radiochemical yields.

Some of the obtained structures lead to good candidates in terms of affinity and selectivity toward other receptors. Autoradiographies and PET imaging has been run and lead to the selection of the best 5-$HT_6$ radioligands.



## IL-A6

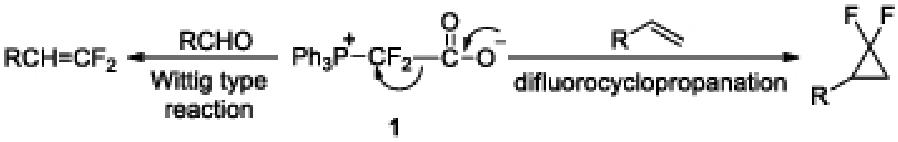
# Synthesis and reaction of some fluorine-containing phosphonium salts

**J.C. XIAO** [(a)]*, **J. ZHENG** [(a)], **J. CAI** [(a)]

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)

* jchxiao@sioc.ac.cn

Phosphonium salts are usually used as the precursors of ylide in Wittig reaction. The ylide is often generated through the dehydrogenation of the phosphonium salts. Therefore, base is usually involved in the Wittig reaction. However, as for the fluorine-containing phosphonium salt like [$Ph_3P^+CF_2H$ $X^-$ ], it is not easy to abstract a proton from a fluorinated carbon. Furthermore, Aldol condensation of the carbonyl compound with α-proton is unavoidable, thus leading to a lower yield or the complex of the reaction under basic conditions. A new phosphonium salt, difluoromethylene phosphobetaine (1), was synthesized. Its structure was characterized and confirmed by X-ray crystal analysis. It was found to be a good precursor of difluoromethylene ylide. The reaction could be conducted under milder conditions without addition of extra base, giving the difluorovinylated product in high yield. Moreover, it was found that this difluoromethylene phosphobetaine could be used as the precursor of difluorocarbene. Difluorocarbene was often produced under harsh reaction conditions. The difluorocyclopropanation or the difluoromethylenation could be performed under milder conditions, which makes the difluoromethylene phosphobetaine a very good difluorocarbene reagent.



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## A6.1

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# Fluoroalkenes Synthesis from Benzothiazolyl Derivatives

**F. LARNAUD** [(a)(b)*], **E. PFUND** [(a)], **B. LINCLAU** [(b)], **T. LEQUEUX** [(a)*]

[(a)] Laboratoire de Chimie Moléculaire et Thioorganique, CNRS UMR 6507 & FR3038, Normandie Université, UNICAEN - CAEN (FRANCE)
[(b)] School of Chemistry, University of Southampton - SOUTHAMPTON (UNITED KINGDOM)

* florent.larnaud@ensicaen.fr
* thierry.lequeux@ensicaen.fr

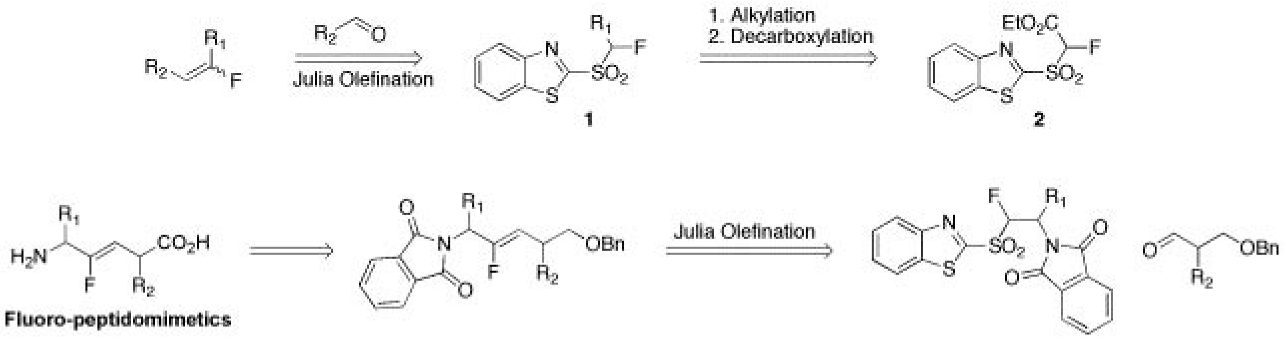
The fluorovinylic moiety has been introduced onto several bio-active compounds such as vitamins, prostaglandins, hormones, pheromones and peptide isosteres [1]. However, access to fluoroalkylidenes is not straightforward and required numerous steps including functionalization of fluoroacrylates easily obtained by HWE reaction.

In 2002, our group described the first one step synthesis of fluoroalkylidene via the modified Julia reaction [2]. Since this report, our main research deals with the preparation of various alkylated fluorobenzothiazolylsulfones as new building blocks for the expeditive synthesis of fluoroalkenes.

For the preparation of alkylfluorosulfones 2, our strategy is based on alkylation reactions under Barbier conditions of benzothiazolylsufonyl fluoroacrylate 1 using alkyl iodides and alcohols, followed by a decarboxylation process carried out under Krapcho conditions [3].

Currently, this approach is applied for on the developement of new peptidomimetics. Indeed, we already reported the expeditive synthesis of fluorinated dipeptide analogues using the modified Julia reaction. Our recent results in this field and the synthesis of biomolecules such as peptide mimics [4] and carbohydrates analogues will be presented.

Acknowledgement
The European Community (INTERREG IVa channel programme, IS:CE-Chem, project 4061) is thanked for financial support.
*ISCE-Chem* has been selected within the scope of the INTERREG IV A France (Channel) – England cross-border European cooperation programme, co-financed by the ERDF.



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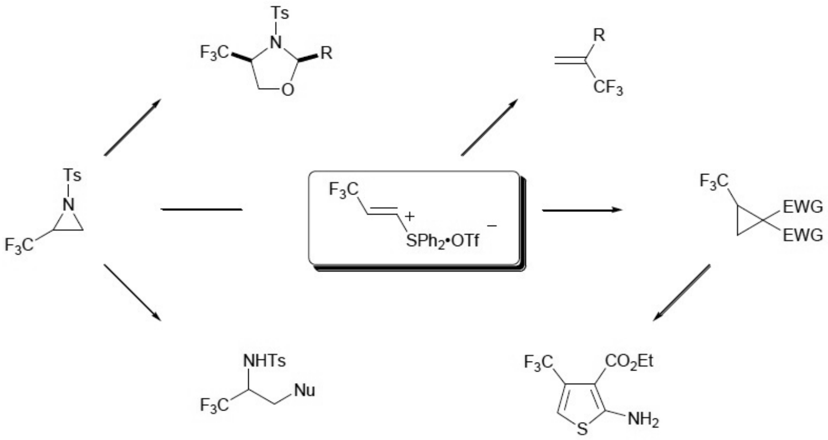
## A6.2

# Synthetic application of ß-(trifluoromethyl)vinyl sulfonium salt

**T. HANAMOTO** [(a)]*, **R. MAEDA** [(a)], **R. ISHIBASHI** [(a)], **N. KASAI** [(a)], **Y. TAKEHIRO** [(a)], **H. FURUNO** [(b)]

[(a)] SAGA UNIVERSITY, DEPARTMENT OF CHEMISTRY AND APPLIED CHEMISTRY - SAGA (JAPAN)
[(b)] Institute for Materials and Engineering (IMCE), Kyushu University - FUKUOKA (JAPAN)

* hanamoto@cc.saga-u.ac.jp



The synthesis of fluorine-containing molecules from fluorine-containing starting materials is called a building block method. The ideal candidate for the fluorinated building block should meet the requirements for being robust, easy-to-handle, and relatively easily available. We selected the title compound and prepared it from 2-bromo-3,3,3-trifluoropropene in high overall yield in two steps. The $CF_3$-containing sulfonium salt well acts as a three-carbon elongation reagent. The synthetic utility is demonstrated in the following examples.

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[3] N. Kasai, R. Maeda, H. Furuno, T. Hanamoto, *Synthesis*, **44** (2012) 3489.

## A6.3

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# Synthesis of Fluorinated Building Blocks by [3,3]-Sigmatropic Rearrangements

**G. HAUFE** [(a)]*, **A. DREIER** [(a)], **D. RAMB** [(a)], **J.S. THRASHER** [(b)]

[(a)] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)
[(b)] Department of Chemistry, Clemson University, Advanced Materials Research Laboratory - ANDERSON, SC (USA)

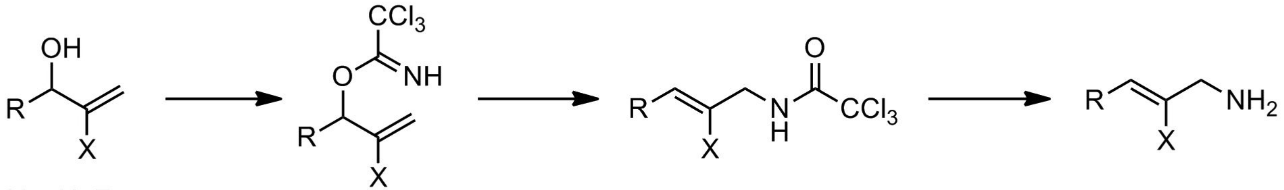
* haufe@uni-muenster.de

A couple of years ago, we described a series of Claisen-type rearrangements of β-fluoroallylic esters. Accordingly α-halo-, α-methyl- and α-aminocarboxylic acid derivatives bearing a vinylic fluorine substituent in 4-position were prepared in good to excellent yields [1-4].

Now we are going to present different protocols of [3,3]-sigmatropic rearrangements to produce fluorinated building blocks. Starting from 2-fluoro-3-hydroxyalk-1-enes of different chain lengths corresponding trichloroacetamidates were synthesized and rearranged in thermal Overman rearrangement to produce, after hydrolysis, 2-fluorinated allylic amines (Scheme 1), which in turn can be used for the preparation of ureas or carbamates.

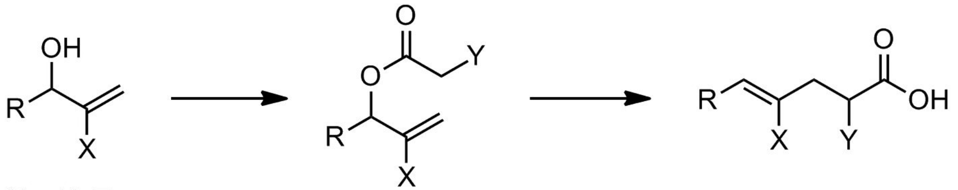
Similarly, the rearrangement of corresponding isocyanates in the presence of amines led to corresponding fluorinated allylic ureas directly.

Furthermore, the Ireland-Claisen rearrangement of allylic esters of 3,3,3-trifluoropropionic acid or pentafluorosulfanylacetic acid deliver α-$CF_3$ or α-$SF_5$-substituted carboxylic acids (Scheme 2).



X = H, F

**Scheme 1**



X = H, F
Y = $CF_3$, $SF_5$

**Scheme 2**

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[1] F. Tranel, G. Haufe, *J. Fluorine Chem.* 125 (2004) 1593-1608.
[2] F. Tranel, R. Fröhlich, G. Haufe, *J. Fluorine Chem.* 126 (2005) 557-569.
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[4] M. Marhold, U. Wittmann, S. Grimme, T. Takahashi, G. Haufe, *J. Fluorine Chem.* **128** (2007) 1306-1317.

# STREAM B

## WEDNESDAY, JULY 24

## IL-B5

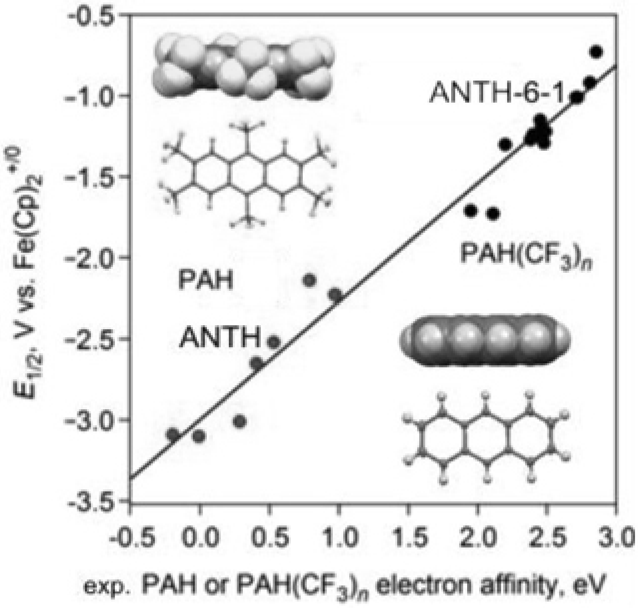
# Fluorocarbon Organic Acceptors: Fundamentals and Applications

**O. BOLTALINA** [(a)]*, **S.H. STRAUSS** [(a)], **I.V. KUVYCHKO** [(a)], **K.P. CASTRO** [(a)], **L.K. SUN** [(a)], **T.T. CLIKEMAN** [(a)], **B.W. LARSON** [(a)], **J.B. WHITAKER** [(a)], **S.N. SPISAK** [(b)], **A.A. POPOV** [(c)], **M.A. PETRUKHINA** [(b)], **S.H.M. DENG** [(d)], **X.B. WANG** [(d)]

[(a)] DEPARTMENT OF CHEMISTRY, Colorado State University - FORT COLLINS (USA)
[(b)] DEPARTMENT OF CHEMISTRY, University at Albany, State University of New York - ALBANY (USA)
[(c)] Department of Electrochemistry and Conducting Polymers, Leibniz Institute for Solid State and Materials Research - DRESDEN (GERMANY)
[(d)] Chemical and Materials Sciences Division, Pacific Northwest National Laboratory - RICHLAND (USA)

* olga.boltalina@colostate.edu

The search for next-generation efficient electroactive organic materials has intensified in recent years due to efforts to modernize currently used light-emitting devices, transistors and renewable-energy devices such as photovoltaic solar cells. Such new materials are expected to lower the production cost, replace rare metals and silicon with materials composed of earth-abundant elements, decrease device weight, and improve durability. It has been well documented that halogenation, and more specifically, fluorination, results in a significant enhancement of electron affinities of organic materials and improves the air stability of electronic devices.



*Correlation of solution $E_{1/2}$ values with gas-phase electron affinities for PAHs and $PAH(CF_3)_n$ compounds*

We have prepared and characterized families of $(C_xH_y)(F)_n$ and $(C_xH_y)(RF)_n$ compounds with $(C_xH_y) = C_{60}$, $C_{70}$, and other fullerenes and with many polycyclic aroma-tic hydrocarbons including corannulene, anthracene, azulene, phenanthrene, pyrene, perylene, and triphenylene, among others. In this lecture, correlations of reduction potentials ($E_{1/2}$) and gas-phase electron affinities ($EA_s$), the most important organic-electron-acceptor figures of merit, with (i) each other (Figure 1 shows one example), (ii) the value of n and the positions of the RF substituents for a given $C_xH_y$ substrate, (iii) different substrates for a given value of n, and (iv) the length of the RF chain for a given $C_xH_y$ substrate and a given value of n, including our most recent work, will be presented and discussed in detail.

## B5.1

# Graphite Intercalation Compounds and Ionic Liquid Crystals based on $(AlF_4)^-$ and Molecular Geometry of $(Al_2F_9)^{3-}$

**K. MATSUMOTO** [(a)]*, **K. TAKAGI** [(b)], **F. XU** [(b)], **R. HAGIWARA** [(a)]
[(a)] KYOTO UNIVERSITY, GRADUATE SCHOOL OF ENERGY SCIENCE - KYOTO (JAPAN)
[(b)] KYOTO UNIVERSITY - KYOTO (JAPAN)
* k-matsumoto@energy.kyoto-u.ac.jp

Fluoroaluminate anions show a variety of unique structures, including monomeric and corner- and edge-sharing oligomeric or polymeric anions [1,2]. In this study, two layered structures based on fluoroaluminate anions, graphite intercalation compounds (GICs) and ionic liquid crystals (ILCs) were prepared and characterized.

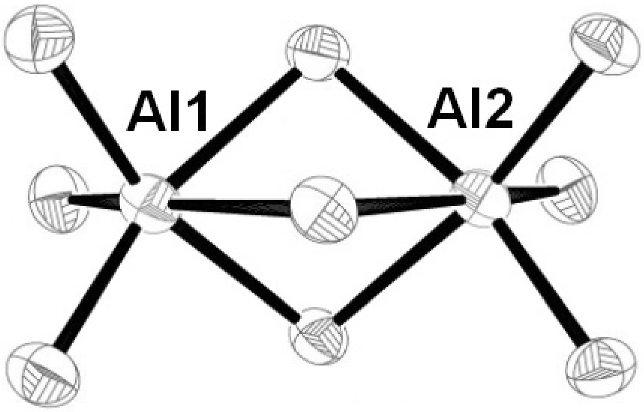


*Fig. 1 The face-sharing $Al_2F_{93}^-$ anion determined in $[C_{18}MI_m]_3[Al_2F_9](CH_2Cl_2)_{1.754}$.*

The GICs of $AlF_4^-$ have been prepared by electrochemical oxidation of a natural graphite electrode in a 1.0 M $CH_3NO_2$ solution of $[N(C_2H_5)_4][AlF_4]$ [3]. The gallery height of the stage-3 GIC (7.9 Å) is in good agreement with the calculated value from the size of $AlF_4^-$ that locates its two-fold axis perpendicular to the graphite layers. Cointercalation of $CH_3NO_2$ is suggested from the composition of the product.

A series of 1-alkyl-3-methylimidazolium tetrafluoroaluminate salts ($[C_xMIm][AlF_4]$, $x$ = 10, 12, 14, 16, and 18) were synthesized by the reaction of $[C_xMIm][AlCl_4]$ with anhydrous HF. The resulting $[C_xMIm][AlF_4]$ salts show ILC phases with $x > 12$. The unique structure of fluoroaluminate anions result an unusual thermal behavior of $[C_xMIm][AlF_4]$ salts, that is, slow structural relaxation. The $Al_2F_9^{3-}$ anion in $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_n$ recrystallized from a $CH_2Cl_2$ solution of $[C_{18}MIm][AlF_4]$ is the first example of a face-sharing fluoroaluminate anion (Fig. 1) [4].

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## B5.2

# A New Generation of Hybrid Carbon-Fluorocarbon Nanocomposite Materials for Electrophysical and Electrochemical Applications

**V. MITKIN** [(a)]*

[(a)] NIKOLAEV INSTITUTE OF INORGANIC CHEMISTRY SB RAS, LAB OF CARBON MATERIALS
CHEMISTRY - NOVOSIBIRSK (RUSSIA)

* mit48@mail.ru

A novel class of porous carbon-fluorocarbon nanocomposites “C – $CF_{1+x}$” (nano-CFCM), have been prepared by mechanochemical activation (MA) of mixed heterogeneous systems “nano-C– nano-$CF_{1+x}$”, having an atomic C:F ratio of 1.14 - 4.0. As nano-carbon, thermally expanded graphite (TEG) and mesoporous carbon material NUMS were used. As nano-$CF_{1+x}$, superstoichiometric fluorocarbons FS and FT ($CF_{1.18\text{-}1.25}$), having ~20-25 Å coherent diffraction area (CDA), 60-70 % of free porosity, 0.1-0.5 wt. % of sum O + $H_2O$ in mixtures, and metals sum < 0.1 wt. % were used.

Data on FTIR, Raman, C1s, O1s, F1s XPS, X-ray diffraction and chemical C,H,F-analyses for various MA-nano-CFCM are given. These are discussed regarding monotonous changes in bulk properties, such as the decrease of C-nanophase relative amounts, decrease of $sp^3$-C-F and $sp^3$-$CF_2$-groups in FS and FT, and occurrence of $sp^3$-C-F-groups in nano-CFCM, which are typical for $C_2F$-like structures. Changes in specific surface of nano-CFCM corresponds to a decrease in CDA sizes and density for all the products. Despite to its low content, the oxygen presence (mainly as $H_2O$) in starting materials has a key influence to interactions in nano-“C-$CF_{1+x}$” systems in MA-processing,. Changes in the surface properties of the MA-“C-$CF_{1+x}$” nanocomposites are connected to the origin of the extremal outstanding properties, with a simultaneous appearance of extremas in specific electrophysical properties of nano-CFCM

MA-processing in systems “$CF_{1+x}$ - C” makes a possibility to produce two types of carbon-fluorocarbon nanocomposites – low-ohmic resistive ($10^{-2}$-$10^{3}$ Ohm$_*$cm), high-ohmic resistive and capacitor materials ($10^{4}$ -$10^{12}$ Ohm$_*$cm). Major factors in the production of targeted electrophysical properties are the types of carbon and fluorocarbon materials, ratio of component’s picnometric volumes and MA-duration. On the basis of this concept, new generation of nanocomposite carbon-fluorocarbon electrodes and resistive materials, were developed, tested and patented, having a surface carbon chemical nanocontact based on carbon black, TEG, soot, cokes etc. There materials are important for the creation of new electrodes for Li-cells, photosensors, chemosensors, nano-thermocouples etc. A special interest for such materials, prepared by simple processes, is that “TEG- $CF_x$” nanocomposites are chemically inert and have very high porosity (free volume of open pores - 60-75 %), that makes such nano-CFCM matrices to be suitable for sorption and catalytic technologies.

## B5.3

# Fluorine Meets buckybowls

**B.M. SCHMIDT [a], B. DUDA [a], B. TOPOLINSKI [a], S. SEKI [b], H. SAKURAI [c], D. LENTZ [a]***

[a] FREIE UNIVERSITÄT BERLIN, Institut für Chemie und Biochemie - BERLIN (GERMANY)
[b] Osaka University - OSAKA (JAPAN)
[c] Institute for Molecular Science - OKAZAKI (JAPAN)

* lentz@chemie.fu-berlin.de

The discovery of fullerenes and endohedral fullerenes, graphene and carbon nanotubes commenced the beginning of a new era of carbon-focused chemistry and the development of organic electronics. Geodesic polyarenes became the focus of attention not only because they can be considered as substructures of fullerenes with three-dimensional bowl-shape or the polar end-caps of carbon nanotubes, but also because of their own chemical and physical properties. Corannulene ($C_{20}H_{10}$) [1] and sumanene ($C_{21}H_{12}$)[2] are the best-studied buckybowl compounds and various synthetic routes have been published.

Herein we report the synthesis of buckybowls bearing strong electronwith-drawing groups like F, $CF_3$, $C_2F_3$, $C_6F_5$. [3, 4]

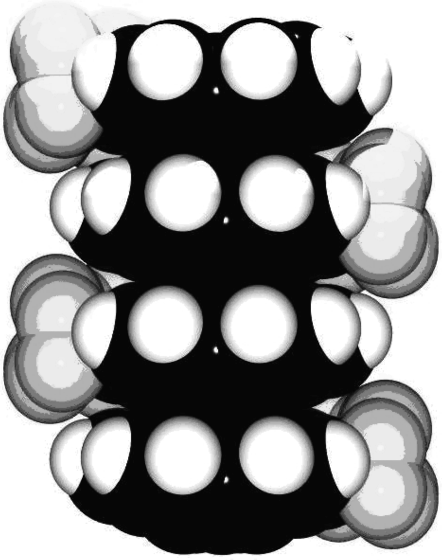

*Fig. 1. Stacking motif of a trifluoromethylated corannulene.*

The electronic and structural properties of new compounds were investigated by UV-vis spectroscopy and cyclic voltammetry. Evaluation of non-covalent interactions in the solid state which generate each structural motif, are supported by single-crystal X-ray diffraction data. Compounds displaying a columnar concave-convex Π-Π-stacking motif will be discussed for possible n-type semiconductor application.

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## IL-B6

# Magnetic Frustration in Vanadium Fluoride-based Kagome Lattices

**P. LIGHTFOOT** [(a)]*

[(a)] UNIVERSITY OF ST ANDREWS, SCHOOL OF CHEMISTRY - ST ANDREWS (UK)

* pl@st-and.ac.uk

Frustrated magnetic systems are currently of great fundamental interest to the condensed matter physics community, as well as an interesting 'design' challenge for the solid state chemist. A particularly sought-after phenomenon is a so-called 'quantum spin liquid' (QSL) state: a non-magnetic ground state in which electron spins are locally paired antiferromagnetically, but there is no long-range magnetic order, even at zero K. Instead, quantum fluctuations over-ride the tendency towards long-range order, and lead to a massively degenerate ground state comprising a superposition of 'resonating' valence-bond pairs [1]. Key features in realising such are state are (i) a geometrically frustrated crystalline lattice (typically triangular in nature) (ii) a layered crystal structure (iii) a 'quantum' spin state, ie. S = ½. The ideal target system is the two-dimensional kagome lattice (Figure 1): a co-planar array of corner-linked equilateral triangles, where every node represents a magnetic ion. Recent work in the field has focussed on various Cu2+ oxide kagome lattices, such as herbertsmithite, Cu3Zn(OH)6Cl2 [2,3]. However, there is still no example of a truly 'ideal' system, since each of the presently known examples contains some deviation from structural or electronic ideality. We have recently focussed our search for new QSL candidates on fluoride-based systems, particularly those based on the $S = ½$ system $V^{4+}$ ($d^1$). We have used ionothermal synthesis to prepare the first example of a $S = ½$ kagome lattice based on a $d^1$ (rather than $d^9$) ion, in the hybrid compound $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ [4]. This compound shows no evidence of magnetic order down to 40 mK (!) despite having strong antiferromagnetic interactions (Weiss constant ~ -80 K), and is therefore a strong candidate for a new paradigm QSL material. In this talk we shall discuss the chemistry, crystallography and physical characterisation of this compound, and also our ongoing attempts to prepare further examples of $V^{4+}$ fluoride based QSL candidates.

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## B6.1

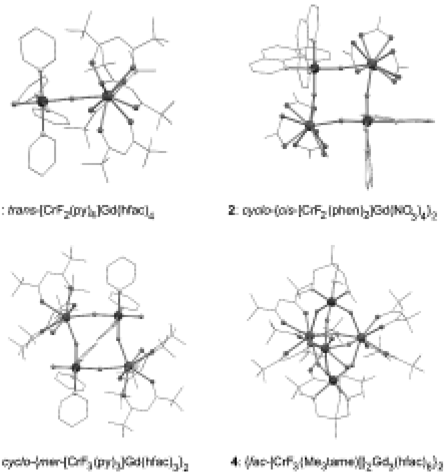
# Fluoride-based modules for molecular magnetic materials

**K. PEDERSEN** [(a)]*, **J. BENDIX** [(a)], **R. CLÉRAC** [(b)]

[(a)] University of Copenhagen, University of Copenhagen - COPENHAGEN (DENMARK)
[(b)] Centre de Recherche Paul Pascal - PESSAC (FRANCE)

* kaspersteenpedersen@gmail.com

A controlled way of combining relevant/interesting physical properties is important in targeting new magnetic materials. Coordination chemistry, in principle, proffers the possibility to delicately tune the properties of modules (or building blocks) and subsequently acquire synthetic topological control. A shortcut to obtaining the desirable control is to remove or block some of the many degrees of freedom in reactivity of a metal ion unit. For a bridging ligand, the simplest conceivable geometrical requirement would be that of a preference for linear bridging. This is found for the ubiquitous cyanide bridges, but also to quite some extent for oxide and fluoride. Several new fluoride-based modules of *n*d transition elements have been synthesized, characterized and assembled by linear μ-fluoride bridging with d- or f-block elements into magnetic polynuclear complexes (including "single-molecule magnets") and one-dimensional systems (including "single-chain magnets"). Thus, for example, reactions of simple lanthanide compounds with various Cr(III)-fluoride complexes yield an extensive series of polynuclear, fluoride-bridged 3d–4f complexes in which the final topology of the material is directed by the structure of the Cr(III) precursor; giving for instance molecular rods, squares or pyramids (see Fig. 1) [1-3].



1: *trans*-[CrF$_2$(py)$_4$]Gd(hfac)$_4$

2: cyclo-(*cis*-[CrF$_2$(phen)$_2$]Gd(NO$_3$)$_4$)$_2$

3: *cyclo*-(*mer*-[CrF$_3$(py)$_3$]Gd(hfac)$_3$)$_2$

4: (*fac*-[CrF$_3$(Me$_3$tame)]$_2$Gd$_3$(hfac)$_6$)$_2$

*Selection of structural motifs obtained from simple lanthanide salts and fluorido-chromium(III) modules.*

All the resulting, structurally simple, systems have allowed for modeling of the magnetic properties and for the first quantification of magnetic coupling between 3d and 4f (and 3d-5d) centers across a fluoride bridge, for orbitally degenerate as well as for orbitally non-degenerate 4f systems. These results are supported by use of a plethora of spectroscopic techniques (inelastic neutron scattering, high-field EPR spectroscopy,...) which, additionally, have been employed to study strong magnetic anisotropy in 5d homoleptic fluorido-complexes.

Conclusively, the modular approach towards low-dimensional molecular magnetic materials has been strongly dominated by cyanide chemistry, but our recent results suggest that a synthetic approach relying on fluoride-based building blocks constitute a convenient, and unexplored, route to magnetically interesting, molecular systems.

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## B6.2

# Unusually Strong Antiferromagnetic Superexchange Coupling in Perovskite KAg$F_3$

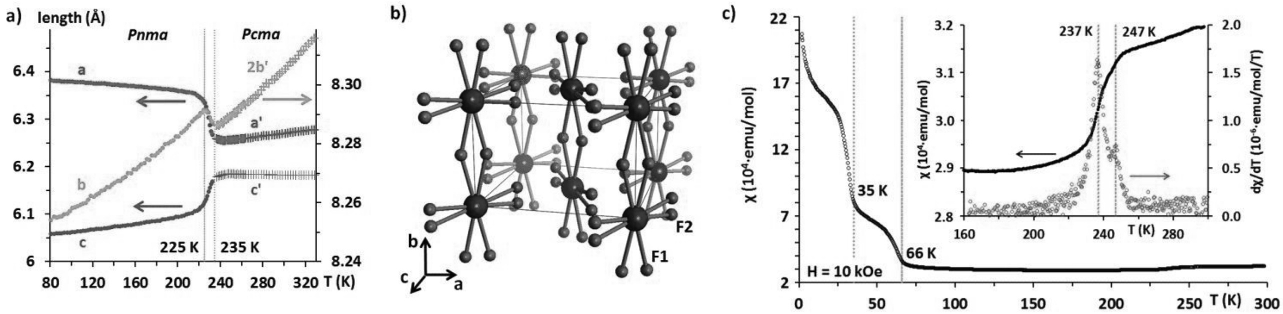
**D. KURZYDLOWSKI** [(a)], **Z. MAZEJ** [(b)], **Z. JAGLICIC** [(c)], **Y. FILINCHUK** [(d)], **W. GROCHALA** [(a)]*

[(a)] Univ. Warsaw, CENT and Fac. Chem. - WARSAW (POLAND)
[(b)] Jožef Stefan Institute, DEPARTMENT OF INORGANIC CHEMISTRY AND TECHNOLOGY - LJUBLJANA (SLOVENIA)
[(c)] University of Ljubljana, and Institute of Mathematic, Physics and Mechanics - LJUBLJANA (SLOVENIA)
[(d)] Univ. Cath. Louvain - LOUVAIN-LA-NEUVE (BELGIUM)

* wg22@cornell.edu

High-purity samples of potassium fluoroargentate(II), $KAgF_3$, have been obtained by a novel synthetic pathway involving controlled thermal decomposition of KAg(III)$F_4$. $KAgF_3$ is found to exhibit an order-disorder phase transition around 230 K. Susceptibility measurements indicate that $KAgF_3$ exhibits strong antiferromagnetic (AFM) coupling reminiscent of to that found in copper(II) oxides. The 1D Ag(II)...F-...Ag(II) superexchange within the 1D $[AgF_2F_{2/2}]^{-1}$ chains is described by constant, J, of the order of -100 meV, with a much weaker ferromagnetic coupling between the chains (theoretical J' = +2.6 meV).

$KAgF_3$ sets a record of the strength of antiferromagnetic superexchange among all fluoride materials known to date.



*Temperature dependence of the cell vectors of $KAgF_3$ (a), the disordered Pcma structure with K atoms omitted for clarity (b); Molar susceptibility of a powdered sample of $KAgF_3$ (c); the inset shows the high-temperature dependence*

## B6.3

# Ion Mobility and Transport Properties of Solid Solutions in the $PbF_2$-Na(Rb)F-$BiF_3$ Systems According to NMR and Conductivity Data

**V. KAVUN** [(a)], **V. KHARCHENKO** [(a)(b)]*, **V. GONCHARUK** [(a)], **I. TELIN** [(a)], **N. UVAROV** [(c)]

[(a)] Institute of Chemistry, FEB RAS - VLADIVOSTOK (RUSSIA)
[(b)] Far Eastern Federal University - VLADIVOSTOK (RUSSIA)
[(c)] Institute of Solid State Chemistry and Mechanochemistry SB RAS - NOVOSIBIRSK (RUSSIA)

* vikharchenko@gmail.com

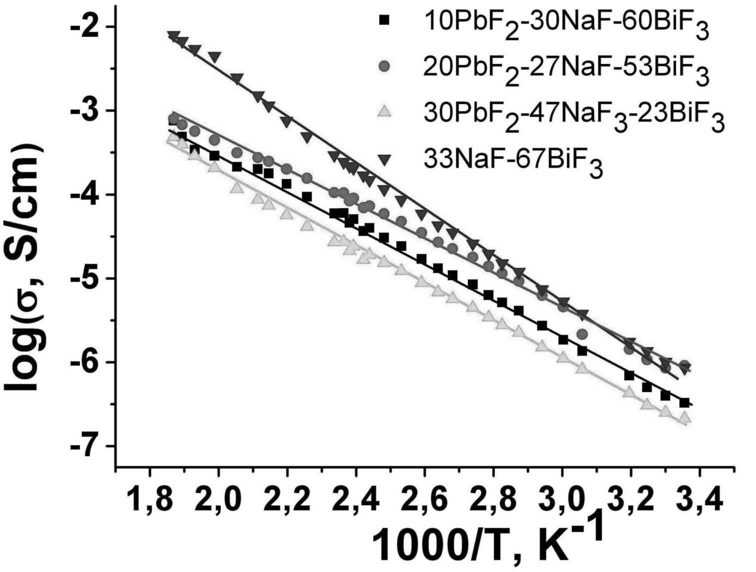


*Fig. Temperature dependence of conductivity of some solid solutions.*

The fluorite-related solid solutions are known to exhibit the fluorine ionic conductivity and may be used as solid electrolytes [1, 2]. The solid electrolytes based on $PbF_2$ and $BiF_3$, such as $MBiF_4$ (M = K, Rb, Tl) and $Pb_{1-x}Bi_xF_{2+x}$, are of special interest due to the high ionic conductivity of about $10^{-2}$ S/cm at 500 K. It is known that in the $PbF_2$-$BiF_3$, KF-$BiF_3$, RbF-$BiF_3$ and NaF–$BiF_3$ systems, the fluorite-type solid solutions of high ionic conductivity are formed, but there are no published data on the ion mobility and transport properties in solid solutions in the $PbF_2$-$BiF_3$-Na(Rb)F ternary systems. As concerns the study of solid solutions in the $PbF_2$-$BiF_3$-KF system, some data were presented in our recent paper [3].

This work presents the research results of ion mobility and ionic conductivity in the fluorite-type solid solutions in the Na(Rb)F–$BiF_3$ and $PbF_2$–$BiF_3$–Na(Rb)F systems.

The presence of diffusion is found in the sodium sublattice of the studied solid solutions. The diffusion intensity depends on the sodium fluoride content in the sample. The observed transformation of $^{19}$F NMR spectra of solid solutions with fluorite structure in the temperature range 150–450 K (single asymmetric line → two-component spectrum → narrow line) is associated with a change in type of ion mobility in the fluoride sublattice at temperature variations: rigid lattice → local motions → translational diffusion of fluorine ions. The temperature range, in which one or another type of ion motion is implemented, is determined by nature of the alkali cation introduced into the solid solution composition in the system $PbF_2$ –$BiF_3$, and also by the concentration of bismuth and lead fluorides.

The electrophysical properties of solid solutions 33NaF–$67BiF_3$, $10PbF_2$–30NaF–$60BiF_3$, $20PbF_2$ –27NaF–$53BiF_3$, $30PbF_2$–47NaF–$23BiF_3$, $50PbF_2$–$30BiF_3$–20NaF, $50PbF_2$–$30BiF_3$–20RbF and $50PbF_2$–$30BiF_3$ –20KF were studied. The specific conductivity of the studied samples is found to depend on their composition and to be in the range $2\times10^{-2} \div 4.4\times10^{-4}$ S/cm at 535 K. The obtained values of conductivity (Fig.) make it possible to consider all the studied solid solutions as a promising basis to create functional materials with high ionic (superionic) conductivity.

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# STREAM C

## WEDNESDAY, JULY 24

## IL-C5

# Innovative Methodology for the Preparation of Quaternary Ammonium Perfluoroalkoxides

**C.M. FRIESEN** [(a)]*, **B.J. JELIER** [(b)], **J.L. HOWELL** [(c)]

[(a)] Trinity Western University, DEPARTMENT OF CHEMISTRY - LANGLEY, BC (CANADA)
[(b)] Simon Fraser University, Department of Chemistry - BURNABY, BC (CANADA)
[(c)] E. I. du Pont de Nemours, Experimental Station - WILMINGTON, DE (USA)

* chad.friesen@twu.ca

With relatively few exceptions, perfluoroalkoxides have been prepared from metal fluoride salts such as M = $K^+$, $Rb^+$, $Cs^+$, and $Ag^+$ with perfluoroacyl fluorides or ketones. The first synthesis of metal-based perfluoroalkoxides was reported by C. J. Willis in 1965 [1]. However, in 1985, W. Farnham used tris(dimethylamino)sulfonium difluorotrimethyl silicate to prepare the first example of the popular sulfur (TAS+) based trifluoromethoxide [2] . Later, the first report of a nitrogen-based cation with $(CF_3)_2CFO^-$ and $CF_3CF_2O^-$ was communicated by K. Seppelt in 1997 [3]. His work required piperidinium fluoride to react with the corresponding perfluoroketone or perfluoroacylfluoride. In 2008, A. A. Kolomeitsev, reported the novel reaction of trifluoromethyl trifluoromethanesulfonate, $CF_3OSO_2CF_3$, with anhydrous tetramethylammonium fluoride to form additional nitrogen-based perfluoroalkoxides [4].

To date, the major challenge in preparing perfluoroalkoxides is the high reactivity and toxicity of the aforementioned starting materials and the inherent propensity for the elimination of metal fluorides. In our recent work, we will report on a method to readily form anhydrous quaternary ammonium perfluoroalkoxides in a single step using relatively inexpensive and easy to use reagents. This methodology would allow for a simple incorporation of fluorinated alkoxides into many synthetic reactions.

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## C5.1

# Versatility in the Functional Properties of Fluorous Triazoles and Tetrazoles

**D.V. FRANCIS** [(a)], **J.B. HARPER** [(a)], **A.I. MOHAMMED** [(a)], **R.W. READ** [(a)*]

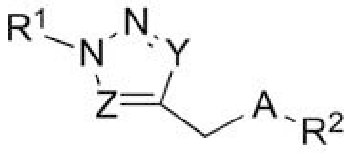
[(a)] University of New South Wales, SCHOOL OF CHEMISTRY - UNSW SYDNEY (AUSTRALIA)

* r.read@unsw.edu.au

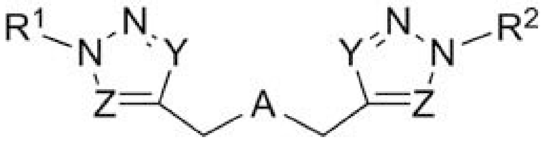
Selective fluorination can impart significant and often beneficial properties on organic molecules, particularly in terms of reactivity and their biological activity. Meanwhile, the extreme hydrophobicity and lipophobicity of highly fluorinated organic molecules very often give them unique physical properties [1-3]. The object of this research has been to design fluorous molecules that possess unique, and preferably defined, physical properties while also being capable of orthogonal functionality.

This paper will describe the development of small libraries of fluorous molecules based on the general structures 1 and 2 (Fig.) [4,5], with one and two heterocyclic core elements, respectively. In this case they are 1,2,3-triazoles and tetrazoles. The heterocyclic scaffolds have been designed (i) to favour the formation of discotic, self-assembled, tertiary structures through pi-pi interactions [6], and (ii) to hold potential for functionality through nitrogen atoms, especially at Y or Z, in response to changes in pH, metal ion, and solvent environments. Such materials have applications as ligands, as biological mimics, and in delivery systems.

Physicochemical and surfactant properties of molecules with A = O, will be described, together with their solution behaviour with changes in pH. Recent progress towards more functionalised molecules with A = $NR^3$ will also be discussed.



**1**



**2**

Y, Z = N or CH

$R^1$, $R^2$ = polyfluoroalkyl, alkyl or polyether group

A = O or $NR^3$

$R^3$ = neutral, *e.g.* H or small alkyl group, or functional

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## C5.2

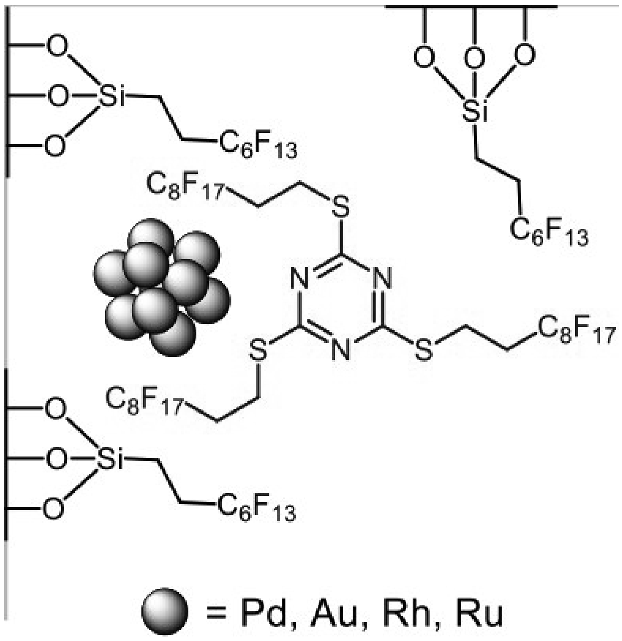
# Perfluoro-tagged metal nanoparticles supported on silica-gel as highly active recoverable catalysts

**A. VALLRIBERA** [(a)]*

[(a)] UNIVERSITAT AUTÓNOMA DE BARCELONA, CHEMISTRY DEPARTMENT - BARCELONA (SPAIN)

* adelina.vallribera@uab.es

Although at first glance heavily fluorinated compounds do not seem best suited as stabilizers of nanoparticles (perfluorinated chains are indeed known to exhibit very small attractive interactions even among themselves), we have demonstrated that fluorinated compounds can be used as protecting shield for nanoparticles. In this context, we observed that previously formed fluorous-stabilized $M_{np}$ were successsfuly immobilized on fluorous silica-gel through fluorous–fluorous interactions or within a silica gel in the form of a hybrid organic-inorganic framework.



Both types of supported $Pd_{np}$-materials can be successfully used as phosphine-free catalysts under air in the copper-free alkynylation of aryl halides in water, in the Suzuki-Miyaura cross-coupling and in the Heck reaction.[1] Excellent recycling of the catalyst (15 cycles in most cases and TONs were obtained). The Heck reaction of aryl halides with allylic alcohols in water is really accessed by this procedure. A two-step one-pot synthesis, involving a Heck reaction followed by an enantioselective enzyme catalyzed reduction to form chiral alcohols is applied in the synthesis of (*R*)-(-)-rhododendrol.[2]

A recyclable gold catalyst was prepared by immobilization of perfluoro-tagged $Au_{np}$ on fluorous silica gel and used in the oxidation of alcohols as well as in domino oxidation/cyclization processes under oxygen atmosphere and solvent-free conditions.[3]

We have extended the benefits of the fluorous hybrid silica to the synthesis of Rh and Ru nanoparticles and used as catalysts for the hydrogenation of arenes in mild conditions.[4]

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## C5.3

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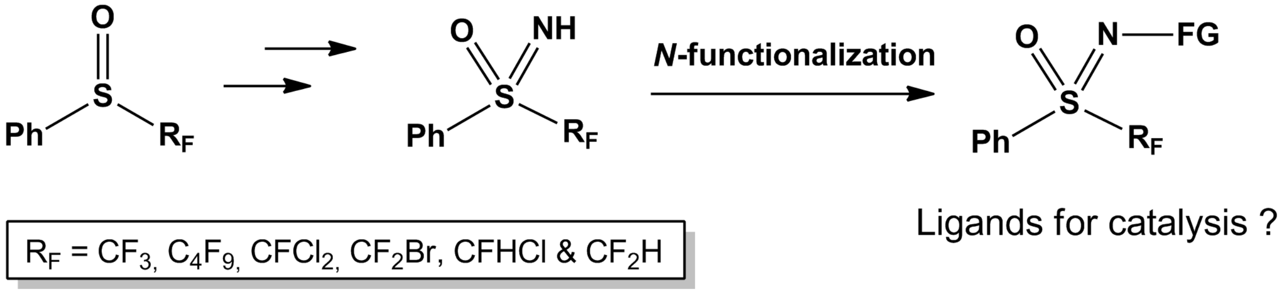
# Fluorinated Sulfoximines as Potential Ligands for Catalysis

**P. DITER [(a)]*, T.N. LE [(a)], E. MAGNIER [(a)], B. PEGOT [(a)], M. TOFFANO [(b)], C. BOURNAUD [(b)], G. VO-THANH [(b)]**
[(a)] ILV, UMR 8180, UNIVERSITÉ DE VERSAILLES, ECHO ÉQUIPE FLUOR - VERSAILLES (FRANCE)
[(b)] ICMMO - ORSAY (FRANCE)
* patrick.diter@uvsq.fr

Sulfoximines bear fascinating and intriguing sulfur (VI) functionality. The extensive variety of existing synthetic methods offers an easy access to these molecules, including their preparation in pure enantiomeric form [1]. These broad synthetic opportunities have stimulated widespread applications for sulfoximines as chiral auxiliary [2], or ligand in asymmetric catalysis [3]. Surprisingly, the field of application is more restricted for *S*-perfluoroalkyl sulfoximines presumably because of their so far cumbersome synthesis. Nevertheless, some recent applications made them very attractive tools. They have been indeed described as very powerful electron withdrawing groups [4], employed for material science purposes [5] and above all, introduced as versatile electrophilic fluoroalkylating reagents[6].

In our laboratory, we have developed a straightforward preparation of fluoroalkylated sulfoximines. Our methodology, in addition to improving the existing synthesis, allows the variation of the $R_F$ chain and gives access to a wide range of free-NH-sulfur (VI) derivatives enabling thus further post-functionalization (Scheme 1).

During this presentation, we will disclose our recent results devoted to the preparation of optically pure sulfoximines and their use as ligands for metal catalysis transformations.



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# STREAM FMEC

## WEDNESDAY, JULY 24

## IL-FMEC6

# The Chemistry of Molten Salt Reactor Fuel

**R. KONINGS [a]*, O. BENEŠ [a]**

[a] EUROPEAN COMMISSION, JOINT RESEARCH CENTER, INSTITUTE FOR TRANSURANIUM
ELEMENTS - KARLSRUHE (GERMANY)

* rudy.konings@ec.europa.eu

The nuclear fuel for the molten salt reactor (MSR) is a ternary or higher order fluoride mixture containing uranium or plutonium as fissile material, thorium as fertile material and other metal fluorides as solvent. In the traditional thermal spectrum MSR, the solvent is the eutectic of LiF and $BeF_2$, whereas for the fast spectrum MSR LiF alone has been suggested. When plutonium is used as fissile material, there is an issue of limited solubility in LiF-$BeF_2$ and other metal fluorides need to be considered. To assess the safety margins of such fuels information is needed on melting point, the actinide solubility, vapour pressure, among others, which are all interlinked via the thermodynamic properties of the molten salt. For that reason we have extensively studied the phase diagrams of the relevant salts with experimental and computational techniques. Due to the specific chemical properties of the fluoride salts (corrosive, volatile, hygroscopic) high temperature experiments cannot be performed with standard techniques, which is further complicated when working with actinides, which are radioactive. In our work we have developed encapsulation techniques for calorimetric that overcome these problems, and allow us to measure liquidus temperature, heat capacity and enthalpy of mixing. In parallel we have used thermodynamic models based on the CALPHAD technique to obtain a consistent multi-compound description of the relevant salts. In this lecture we will of course highlight the work done on the LiF-$BeF_2$-$ThF_4$-$UF_4$ system, the reference system for the MSR, but also on alternative systems and will show the strength of thermodynamic modelling for optimising the composition of the solvent.

## FMEC6.1

# Classification of several fluoride molten salts according to their fluoro-acidity properties

**S. DELPECH** [a]* , **S. JASKIEROWICZ** [a], **D. RODRIGUES** [a]

[a] CNRS-IPN, IPN RADIOCHIMIE - ORSAY (FRANCE)

* delpech@ipno.in2p3.fr

The molten salt fast reactor is one of the six concepts which were selected as a possible concept for the IVth generation of nuclear energy system. The particularity of molten salt reactor is to use a liquid fuel constituted of a fluoride salt mixture with LiF, $ThF_4$, $UF_4$. The chemical issues addressed for this concept are the chemical properties of the salt (on which depend the solubilities and the properties of fission products), the pyrochemical methods required for the spent fuel reprocessing and the control of the redox potential of the fuel salt which insures the structural material resistance. In this work, we were especially interested by the fluoro-acidity of fluoride mixtures and the impact on the solvation of metal fluorides which depends mainly on the activity of fluoride ions. The fluoro-acidity of a molten fluoride salt is related to the activity of free fluoride in the salt [1]. The measurement of such a data is based on indirect methods, one of them consists in the measurement of the equilibrium between dissolved Si(IV) and gaseous Si(IV) in several salt [2]. The aim of this work is to present the results obtained by comparison of potentiometric measurements of the redox system Ni(II)/Ni in several molten salt, the mathematical analysis of the measurements leading to define a function related to fluoro-acidity, this function being only dependent on activity coefficients and on of fluoride ion activity. In this way, a concept of pF indicator electrode was developed [3] providing, through potentiometric measurements, a relative fluoro-acidity scale leading to classify and quantify the acidity of various fluoride mixtures (fig.1). The validation of such a method will be firstly discussed in this work. Secondly, the classification of the several fluoride binary salts will be given, showing that the acidity increases with the complexity of the salts constituting the mixture: $ZrF_4$, $ThF_4$ are more acidic compounds than $AlF_3$ or NaF.

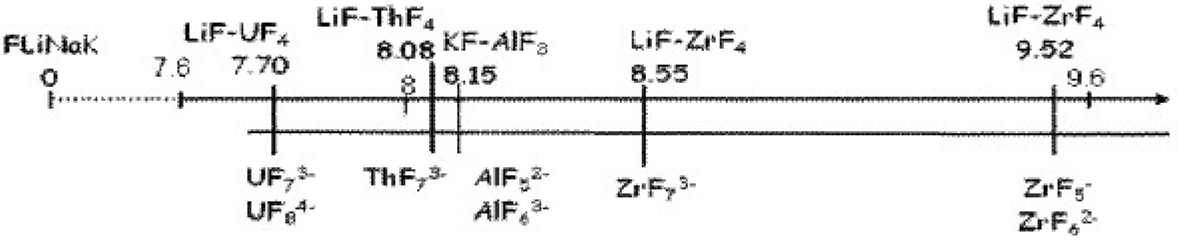

*Figure 1: “Fluoro-acidity” scale.*

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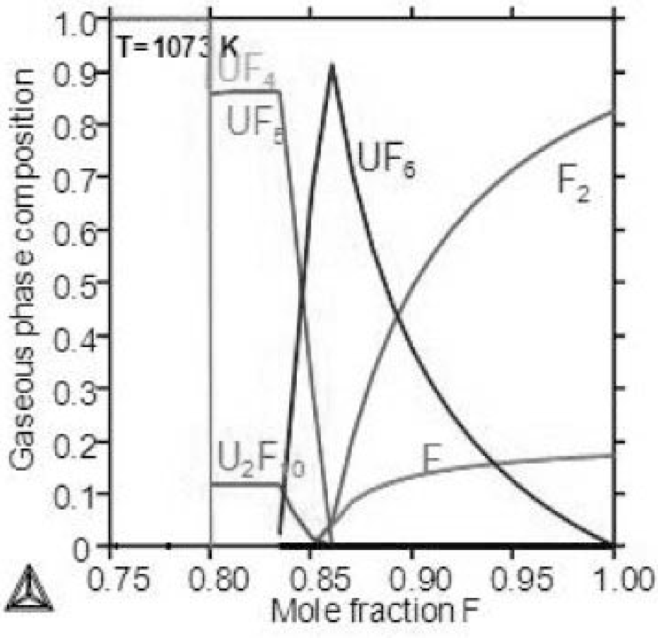
## FMEC6.2

# Thermodynamic contribution to the study of fluoride compounds for front end nuclear cycle

**S. CHATAIN** [(a)]*, **J. FLÈCHE** [(a)], **B. MOREL** [(b)], **C. GUENEAU** [(a)]

[(a)] CEA, DPC/SCCME/LM2T - GIF-SUR-YVETTE (FRANCE)
[(b)] AREVA/COMURHEX - PIERRELATTE (FRANCE)

* sylvie.chatain@cea.fr



In France, the isotopic enrichment of natural uranium is performed by a gas diffusion process using uranium hexafluoride, $UF_6$, which is fabricated by fluoration of uranium tetrafluoride $UF_4$. Uranium fluorides are thus key compounds in the nuclear cycle front end.

The CALPHAD method (CALculation of PHAse Diagram), a thermodynamic approach which couples phase diagram data and thermodynamic properties of chemical systems is used. The Gibbs energies of all the gas, liquid and solid phases are expressed as polynomial functions of temperature and chemical composition. These parameters are optimized using experimental information including melting and other phase transformation temperatures, solubilities, as well as thermodynamic properties (heat capacities, enthalpies of formation, and chemical potentials) but also calculated data using first principle methods.

With such assessed databases, many thermodynamic calculations can be performed like gaseous phase composition (Fig. 1), phase stability domains versus oxygen and/or fluorine potential or phase diagrams. ..

Through examples of investigations of the uranium-fluorine-oxygen (U-F-O), molybdenum-fluorine-oxygen (Mo-F-O), fluorine-potassium-uranium (F-K-U) and fluorine-sodium-uranium (F-Na-U) systems, we will show how such an approach can be useful to understand phenomena occurring in industrial processes and to help the optimization of the experimental conditions in these industrial production studies.

## FMEC6.3

# Investigation of Molten Fluoride Systems Containing Niobium by Electrochemical and Carbothermal Reduction Methods

**S. KUZNETSOV** [(a)]*

[(a)] INSTITUTE OF CHEMISTRY, KOLA SCIENCE CENTRE RAS, HIGH TEMPERATURE CHEMISTRY AND ELECTROCHEMISTRY - APATITY (RUSSIA)

* kuznet@chemy.kolasc.net.ru

Pyrochemical reprocessing involving fluoride molten salts could represent a promising alternative to the aqueous separation methods. Niobium is a fission product and knowledge of niobium chemistry and electrochemistry is very useful for the recycling of spent nuclear fuel.

The aim of the present work is study of the second coordination sphere influence on the diffusion coefficients of niobium complexes, the standard rate constants of charge transfer ($k_s$) for the Nb(V)/Nb(IV) redox couple and investigation of the working electrode nature on kinetics of the redox reaction.

The diffusion coefficients of Nb(V) and Nb(IV) complexes in NaF-KF, KF, CsF melts were determined by cyclic voltammetry, chronopotentiometry and chronoamperometry methods. The values determined by these methods are in a good agreement with each other. It was found that logarithms of Nb(V) and Nb(IV) diffusion coefficients linearly depend on the reciprocal value of alkali metal cation radius and the diffusion coefficients decrease with changes in the composition of the second coordination sphere from sodium to cesium.

The standard rate constants increased with increasing temperature and values of $k_s$ obtained at a platinum electrode were higher than those at a glassy carbon electrode. .The values of $k_s$ change in series Cs < K < Na and magnitudes of $k_s$ testify that the redox process proceeds quasi-reversibly.

Influence of oxide ions on electrochemical behavior of niobium in fluoride melts was studied.

By carbothermal reduction method using Leco TC-436 the oxide content in quenched samples of LiF-NaF-KF (FLiNaK) eutectic melt was determined. It was found that in FLiNaK containing oxofluoride compounds of niobium two sources of oxygen are exist. The first corresponds to free $O^{2-}$ and the second one to $O^{2-}$ in the composition of oxofluoride complexes. The ratio between different forms of oxygen depends on the ratio O/Nb in the melt.

Data of Leco-analysis on coexistence of oxygen in two different forms were confirmed by electrochemical studies.

The work was financially supported by the Russian Foundation for Basic Research (project 12-08-01178-a).

# THURSDAY, JULY 25

# THURSDAY, JULY 25

## Morning 9:00 – 10:30

## STREAM A

**CHAIR:** E. MAGNIER, ***Université de Versailles St Quentin, Versailles (France)***

**9:00** **IL-A7** **Invited Lecture**

**A NOVEL NON CATALYTIC C-H PERFLUOROALKYLATION OF AROMATIC SUBSTRATES BY $RfSiMe_3$ BASED ON ACTIVATION OF π-SYSTEM**

**Y. Yagupolskii,** N. V. Kirij, K. Y. Zabolotny, A. Filatov

*Institute of Organic Chemistry, NAS of Ukraine, Kyiv (Ukraine)*

**9:30** **A7.1** **SYNTHESIS OF HIGHLY FUNCTIONALISED MONOFLUORINATED CYCLOPROPANES**

**P. Ivashkin**, S. Couve-Bonnaire, P. Jubault, X. Pannecoucke

*INSA Rouen, UMR 6014, Mont Saint-Aignan (France)*

**9:50** **A7.2** **ENANTIOSELECTIVE CONSTRUCTION OF FLUORINATED CHIRAL CARBON CENTERS**

**K. Shibatomi**

*Toyohashi University of Technology, Dept of Environmental & Life Sciences (Japan)*

**10:10** **A7.3** **DIRECT ALDOL-REDUCTION PROCESS USING DIFLUOROMETHYL ARYL KETONES AND ARYL ALDEHYDES IN THE PRESENCE OF POTASSIUM *TERT*-BUTOXIDE: ONE-POT EFFICIENT STEREOSELECTIVE SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL *ANTI*-2,2 DIFLUOROPROPANE-1,3 DIOLS**

W. Xu, W. Muramatsu, M. Bellance, G. Pilet, W. Dolbier Jr, **M. Médebielle**

*Université Claude Bernard Lyon1, ICBMS (France)*

## STREAM B

**CHAIR:** **W. GROCHALA**, *University of Warsaw, CENT & Faculty of Chem, (Poland)*

**9:00** **IL-B7** **Invited Lecture**

**RARE EARTH DOPED INORGANIC FLUORIDE MATERIALS: SYNTHESIS AND APPLICATIONS**

**M. Mortier,** P. Aballea, H. Serrier-Brault, T. Dheivasigamani, L. Michely, P. Gredin, G. Patriarche

*ENSCP-CHIMIE PARISTECH, LCMCP, PARIS (FRANCE)*

**9:30 B7.1** **PROGRESS IN FLUORIDE LASER CERAMICS**
**P. Fedorov,** M. Doroshenko, E. Garibin, V. Osiko
*Prokhorov General Physics Institute, RAS, Laser Materials & Technology Research Center, Moscow (Russia)*

**9:50 B7.2** **NOVEL CATIONIC IRIDIUM COMPLEXES FOR BLUE PHOSPHORESCENT OLEDS**
**Y. Takahira**, E. Murotani, K. Fukuda
*Asahi Glass Co., Ltd., Research Center, Yokohama-Shi (Japan)*

**10:10 B7.3** **SYNTHESIS AND LUMINESCENT CHARACTERISTICS OF $NaYF_4$:Yb:Er POWDERS FOR PHOTODYNAMIC CANCER THERAPY**
**S. Kuznetsov**, D. Yasirkina, N. Ryabova, D. Pominova, P. Fedorov, V. Voronov, O. Uvarov, V. Osiko, A. Baranchikov
*A.M. Prokhorov General Physics Institute - RAS, Technology of Nanomaterial for Photonics, Moscow (Russia)*

## STREAM FMEC

**CHAIR: K. AMINE,** ***Argonne National Laboratory, Argonne (USA)***

**9:00 IL-FMEC.7** **Invited Lecture**
**F-BASED MATERIALS FOR Li-ION BATTERIES**
**J. M. Tarascon**
*Université de Picardie - Jules Verne, LRCS, Amiens (France)*

**9:30 FMEC7.1** **ELECTROCHEMICAL PROPERTIES OF THERMALLY ACTIVATED $Li_3FeF_6$ AS A CATHODE MATERIAL IN LITHIUM SECONDARY CELLS**
**A. Basa**, K. Pietrowska, M. Perkowski, S. Wojtulewski, A. Z. Wilczewska, E. Gonzalo, A. Kuhn, F. Garcia-Alvarado
*University of Bialystok, Institute of Chemistry (Poland)*

**9:50 FMEC7.2** **SYNTHESIS OF $LiFePO_4F$ BY SOLID-GAZ REACTION : REVISITING THE CERAMIC METHOD**
**P. Bonnet**, R. Kemogne-Debah, N. Louvain, L. Frezet, C. Fonquernie, M. El-Ghozzi, K. Guerin, B. Devouard, P. Willmann
*Université Blaise Pascal - Clermont2, Institut de Chimie de Clermont Ferrand, Aubière (France),*

**10:10 FMEC7.3** **REMARKABLE TRANSFORMATION OF FLUORINE FROM A SMALL EXOTIC ELEMENT INTO HIGHLY VALUED AND MATURE PARTICIPANT IN ENERGY CONVERSION AND STORAGE SYSTEMS**
**D. Meshri,** N.C. Mathur, R. Adams, S. Meshri, R. Jain, D. Pinnapareddy
*Advance Research Chemicals Inc., Catoosa, OK (USA)*

**10:30 – 11:00** *Coffee*

# Morning 11:00 – 12:30

## STREAM A

CHAIR: H. KORONIAK, *Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

**11:00 IL-A8** Invited Lecture

CONVENIENT STEREOSELECTIVE SYNTHESIS OF β-PERFLUOROALKYL-β-ALKYL α,β-UNSATURATED ESTERS

**T. Yamazaki**

*Tokyo University of Agriculture & Technology, Institute of Engineering, Division of Applied Chemistry, Koganai (Japan)*

**11:30 A8.1** REACTIONS OF CHIRAL ALKYL AND ARYL TRIFLUOROMETHYL N-*TERT*-BUTANESULFINYLHEMIAMINALS WITH ORGANOMETALLIC REAGENTS

**F. Grellepois**

*Université de Reims-Champagne-Ardenne, ICMR UMR7312 CNRS (France)*

**11:50 A8.2** ASYMMETRIC ORGANOCATALYTIC SYNTHESIS OF CHIRAL TRIFLUOROMETHYLATED HETEROCYCLES

**V. Sukac**, V. Tkachuk, V. Shoba, M. Vovk

*Institute of Organic Chemistry NASU, Laboratory, Kyiv (Ukraine)*

**12:10 A8.3** ENANTIOSELECTIVE SYNTHESIS OF EPOXIDES HAVING A TETRASUBSTITUTED TRIFLUOROMETHYLATED CARBON CENTER: METHYLHYDRAZINE-INDUCED AEROBIC EPOXIDATION OF BETA,BETA-DISUBSTITUTED ENONES

**N. Shibata**

*Nagoya Institute of Technology, Dept of Frontier Materials (Japan)*

## STREAM B

CHAIR: M. GERKEN, *University of Lethbridge, Lethbridge (Canada)*

**11:00 IL-B8** Invited Lecture

NEW DEVELOPMENTS IN SYNTHETIC AND STRUCTURAL NOBLE-GAS CHEMISTRY; THE COORDINATION BEHAVIORS OF $NgF_2$ (Ng = Kr, Xe) TOWARDS METAL AND NON-METAL CENTERS; AND THE SYNTHESES OF $FXeOXO_3$ (X = Cl, Br) AND RELATED $XO_2^+$ COMPLEXES OF $NgF_2$

**G.J. Schrobilgen**, U. Breddemann, J. Haner, D. S. Brock, H.P.A. Mercier, M. Ellwanger, J.R. DeBackere, M. Lozinšek, B. Žemva

*Dept. of Chemistry, McMaster University, Hamilton, ON (Canada)*

**11:30 B8.1** **INFINITE INSULATED π -STACKED DONOR/ACCEPTOR MOLECULAR ARRAYS: $^{-}$[PAH′/PAH($CF_3$)$_n$]$_\infty$$^{-}$ CHARGE-TRANSFER CO-CRYSTALS**
I. V. Kuvychko, K. P. Castro, E. V. Bukovsky, O. Boltalina, Y. S. Chen, **S.H. Strauss**
*Colorado State University, Dept of Chemistry, Fort Collins, CO (USA)*

**11:50 B8.2** **COMPLEXES OF CYCLIC π-PERIMETERS WITH PERFLUORINATED VINYL SIDE CHAINS**
**D. Heinrich**, D. Lentz
*FU Berlin, Anorganische Chemie (Germany)*

**12:10 B8.3** **“$XeF_2$ RICH” AND “$XeF_2$ POOR” COMPOUNDS IN THE SYSTEM $XeF_2$ – $TiF_4$**
**K. Radan,** E. A. Goreshnik, B. Žemva
*Jožef Stefan Institute, Dept of Inorganic Chemistry & Technology, Ljubljana (Slovenia),*

## STREAM FMEC

**CHAIR: J.-M. TARASCON, *Université de Picardie – Jules Vernes, Amiens (France)***

**11:00 IL-FMEC8** **Invited Lecture**
**BATTERIES BASED ON METAL HALIDES**
**M. Fichtner,** M. A. Reddy, B. Breitung, V. S. K. Chakravadhanula, B. K. Das, C. Rongeat, D. Wang, X. Zhao
*Karlsruhe Institute of Technology -HIU-, Karlsruhe (Germany)*

**11:30 FMEC8.1** **EFFECT OF SURFACE FLUORINATION ON THE CHARGE/DISCHARGE PROPERTIES OF HIGH POTENTIAL NEGATIVE ELECTRODE $TiO_2$(B) FOR LIBs**
**A. Tasaka**, M. Saito, Y. Nakano, M. Takagi, T. Maekawa, H. Takebayashi, Y. Shodai, M. Inaba
*Doshisha University, Kyoto (Japan)*

**11:50 FMEC8.2** **TITANIUM OXYFLUORIDE HAVING THE ANATASE TYPE STRUCTURE: SHORT-LONG RANGE ORDERS AND ELECTROCHEMICAL PROPERTIES**
**D. Dambournet**, W. Li, D. Corradini, M. Salanne, A. L. Rollet, C. Julien, H. Groult, K. Zhagib, C. Legein, M. Body, K. Chapman, P. Chupas
*Université Pierre & Marie Curie, Laboratoire PECSA, Paris (France)*

**12:10 IL-FMEC9** **Invited Lecture**
**NEW FLUORINE-CONTAINING CATHODE MATERIALS FOR Li-ION BATTERIES**
**E. Antipov**, N. Khasanova, O. Drozhzhin
*Moscow State University, Dept of Chemistry (Russia)*

**12:30 – 13:30** *Lunch*

# Afternoon 14:00 – 15:30

## STREAM A

CHAIR: F. GRELLEPOIS, *Université de Reims–Champagne-Ardenne, Reims (France)*

**14:00 IL-A9** Invited Lecture

NEW TRANSFORMATIONS OF FLUORINATED ALKYNES MEDIATED BY TRANSITION METALS

**C. Del Pozo,** S. Fustero

*University of Valencia, Dpto. Q. Orgánica, Burjassot (Spain)*

**14:30 A9.1** PD-CATALYZED *ORTHO*-SELECTIVE C-F ACTIVATION OF POLYFLUROARENES

Z. Chen, C. He, **X. Zhang**

*Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, CAS (China)*

**14:50 A9.2** OXIDATIVE TRIFLUOROMETHYLATION OF UNACTIVATED OLEFINS WITH $CF_3SiMe_3$

**F. L. Qing**

*Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, CAS (China)*

**15:10 A9.3** PROSPECTS OF SYNTHETIC ELECTROCHEMISTRY IN THE DEVELOPMENT OF NEW METHODS OF ELECTROCATALYTIC FLUOROALKYLATION

**Y. Budnikova**, D. Vicic, Y. Dudkina, D. Mikhailov, M. Khrizanforov, T. Gryaznova

*A.E. Arbuzov Institute of Organic & Physical Chemistry, Electrochemical Synthesis Lab., Kazan (Russia)*

## STREAM B

CHAIR: S. BRUNET, *Université de Poitiers, Poitiers (France)*

**14:00 IL-B9** Invited Lecture

RECENT ADVANCES IN DEVELOPING NEW LOW GWP ALTERNATIVES TO HFC & HCFC

**M. Nappa**

*E. I. DuPont de Nemours & Co., Experimental Station, Wilmington, DE (USA)*

**14:30 B9.1** ENVIRONMENTAL CHEMISTRY OF ULTRA-LOW GWP FLUOROCARBONS
**R. Singh**
*Honeywell International, Fluorine Products, Buffalo, NY (USA)*

**14:50 B9.2** MODERATE LEWIS ACID METAL FLUORIDE WITH HIGH SPECIFIC SURFACE AREA AS CATALYST FOR THE FLUORINATION OF 2-CHLOROPYRIDINE BY HF
**A. Astruc**, S. Celerier, S. Brunet
*Université de Poitiers, IC2MP UMR7285 (France)*

**15:10 B9.3** FLUORINATION CATALYSIS FOR HALOGEN EXCHANGE CHEMISTRY IN THE PREPARATION OF LOW GLOBAL WARMING POTENTIAL (L-GWP) FLUOROCARBONS
S. Seshadri, **R. Syvret**
*Arkema Inc., Fluorochemicals R&D, King of Prussia, PA (USA)*

# STREAM FMEC

**CHAIR: T. NAKAJIMA, *Aichi Institute of Technology, Toyota (Japan)***

**14:00 IL-FMEC10** **Invited Lecture**
NOVEL LOW EW, WATER INSOLUBLE PERFLUORO-SULFONIMIDE (PFSI) IONOMERS
**J.S. Thrasher,** A. V. Matsnev, T.S. Sayler, R. E. Fernandez, A. Waterfeld
*Clemson University, Advanced Materials Research Laboratory, Dept of Chemistry, Anderson, SC (USA)*

**14:30 FMEC10.1** NANO-STRUCTURED AROMATIC IONOMERS PARTIALLY FLUORINATED FOR PEMFC
**L. Assumma**, C. Iojoiu, R. Mercier , S. Lyonnard
*Université de Grenoble, LEPMI (France)*

**14:50 FMEC10.2** NOVEL BLEND MEMBRANES FOR PEMFC BASED ON S-PEEK AND FLUORINATED COPOLYMERS BEARING AZOLE (IMIDAZOLE, BENZIMIDAZOLE OR TRIAZOLE) COMPOUNDS: A STUDY ON N-HETEROCYCLE NATURE
**B. Campagne,** D. Ghislain, B. Ameduri, D. J. Jones, R. Jacques, I. Roche
*Institut Charles Gerhardt- Ecole Nationale Supérieure de Chimie de Montpellier (France)*

**15:10 FMEC10.3** CHARACTERIZATION BY MICRO-RAMAN SPECTROSCOPY OF TRI-LAYER PFSA MEMBRANE FOR PEM FUEL CELLS
**C. Bas**, J. Guironnet, A. El Kaddouri, E. Moukheiber, G. De Moor, L. Flandin
*Université de Savoie, LEPMI - UMR5279, Le Bourget du Lac (France)*

**15:30 – 15:50** *Coffee*

# Afternoon 15:50 – 17:40

## STREAM A

**CHAIR**: **N. SHIBATA**, ***Nagoya Institute of Technology, Nagoya (Japan)***

**15:50** **IL-A10** **Invited Lecture**
**FLUORINATION IN SUPERACID HF/SbF$_5$**
**S. Thibaudeau**
*Université de Poitiers, Superacid group - Organic Synthesis team - UMR 7285 IC2MP (France)*

**16:20** **A10.1** **HYDROGEN-BOND DONATION PROMOTES C-F BOND ACTIVATION FOR NUCLEOPHILIC SUBSTITUTIONS ON ACTIVATED ALKYL FLUORIDES**
**P.A. Champagne**, Y. Benhassine, J.E. Paquin
*Université Laval, Québec (Canada),*

**16:40** **A10.2** **DFT STUDY ON FLUOROALKENE METATHESIS: THE ROLE OF PRODUCTIVE AND NON-PRODUCTIVE CYCLES**
**J. Kvicala**, M. Rybackova, J. Hosek, O. Simunek
*Institute of Chemical Technology, Dept of Organic Chemistry, Prague (Czech Republic)*

**17:00** **A10.3** **SYNTHESIS AND APPLICATIONS OF PENTAFLUORO-SULFANYLDIFLUOROACETIC ACID**
**A.V. Matsnev**, M. A. Stanton, S. Qing, G. Haufe, J. S. Thrasher
*Clemson University, Advanced Materials Research Laboratory, Dept. of Chemistry, Anderson (USA)*

17:20 A10.4 **SYNTHESIS AND CATALYSIS OF FLUORINATED ORGANIC BRØNSTED ACIDS**
**H. Yanai**, T. Yoshino, N. Ishii, T. Taguchi
*Tokyo University of Pharmacy & Life Sciences, School of Pharmacy, (Japan)*

## STREAM B

**CHAIR**: **K. O. CHRISTE**, ***University of Southern California, Los Angeles (USA)***

**15:50** **IL-B10** **Invited Lecture**
**TRIPLE BOND SYSTEMS OF SULFUR**
**R. Mews,** T. Bormann, E. Lork, W.-D. Stohrer, H.Oberhammer
*University of Bremen, Dept of Chemistry (Germany)*

**16:20** **B10.1** **REACTIONS OF SF$_4$ AND SF$_3^+$ WITH LEWIS BASES**
P. Chaudhary, J. Goettel, H. Mercier, P. Hazendonk, **M. Gerken**
*University of Lethbridge, Dept of Chemistry & Biochemistry, Alberta (Canada)*

**16:40 B10.2** STRUCTURES OF AROMATIC RADICAL CATIONS
**K. Seppelt**, M. Khanfar, M. Molski, H. Shorafa
*FU Berlin, Institut Chemie und Biochemie (Germany)*

**17:00 B10.3** PENTAFLUOROETHYLTINFLUORIDE AND BIS(PENTAFLUOROETHYL)STANNYLENES
**J. Klösener**, B. Hoge
*Bielefeld University, Inorganic Chemistry (Germany)*

**17:20 B10.4** PROTONATION OF UREA AND THIOUREA IN SUPERACIDS
**A. Kornath**, J. Axhausen, K. Lux
*Ludwig-Maximilian University, Dept of Chemistry, Munich (Germany)*

# STREAM FMEC

CHAIR: **J. THRASHER**, ***Clemson University, Anderson (USA)***

**15:50 IL-FMEC11** **Invited Lecture**
ARKEMA'S ADVANCES IN FLUOROCHEMICAL TECHNOLOGIES FOR LITHIUM ION BATTERY
**P. Bonnet,** G. Schmidt, J. Chauveau
*Arkema, Centre de Recherches Rhône-Alpes, Pierre-Bénite (France)*

**16:20 FMEC11.1** SAFETY IMPROVEMENT OF LITHIUM ION BATTERY BY FLUORINE COMPOUNDS HAVING LOW REACTIVITY WITH Li AND HIGH OXIDATION STABILITY
**T. Nakajima**, D. Nishikawa, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, H. Aoyama
*Aichi Institute of Technology, Dept of Applied Chemistry, Toyota (Japan)*

**16:40 FMEC11.2** SYNTHETIC APPROACHES FOR NEW COMPONENTS OF LITHIUM BATTERY ELECTROLYTES
T. Boettcher, N. Kalinovich, O. Kazakova, K. Vlasov, M. Ponomarenko, R. Schmitz, M. Winter, **G. Roeschenthaler**
*Jacobs University, School of Engineering & Science, Bremen (Germany)*

**17:00 FMEC11.3** SINGLE-ION BAB TRIBLOCK COPOLYMERS AS HIGHLY EFFICIENT ELECTROLYTES FOR LITHIUM-METAL BATTERIES
**R. Bouchet,** A. Aboulaich, S. Maria, R. Meziane, J-P Bonnet, M. Armand, L. Lienafa, T. N. T. Phan, D. Bertin, D. Gigmes, R. Denoyel
*Institut Polytechnique de Grenoble, LEPMI–Phelma (France)*

**17:20** **IL-FMEC12** **Invited Lecture**

**ADVANCED NEXT GENERATION HIGH ENERGY LITHIUM BATTERY**

**K. Amine**, H. Wu, Z. Chen, I. Belharouak, Z. Zhang, W. Wei, J. Yang, A. Abouimrane, Y. K. Sun

*Argonne National Laboratory, Chemical Sciences & Engineering Div., Argonne (USA)*

**17:40** **CONCLUSIONS & FAREWELL PARTY**

# STREAM A

## THURSDAY, JULY 25

## IL-A7

# A novel non-catalytic C-H perfluoroalkylation of aromatic substrates by RfSi$Me_3$ based on activation of π-system

**Y. YAGUPOLSKII** [(a)]*, **N.V. KIRIJ** [(a)], **K.Y. ZABOLOTNY** [(a)], **A. FILATOV** [(a)]

[(a)] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Organofluorine department - KYIV (UKRAINE)

* Yagupolskii@ioch.kiev.ua

A novel non-catalytic C-H perfluoroalkylation methodology of aromatic substrates by $R_f$Si$Me_3$ based on strong activation of aromatic π-system by electron withdrawing substituents or by organometallic tripod in arene tricarbonyls will be presented.

The last approach recently developed offers convenient and mild possibility to form cyclohexadienyl-metal complexes with Rf-group attached to six member ring ligand. Subsequent mild oxidation leads to perfluoroalkyl containing arenes. Reaction sequence may be performed in one-pot variant.

Scope and limitations of the methodology found will be discussed.

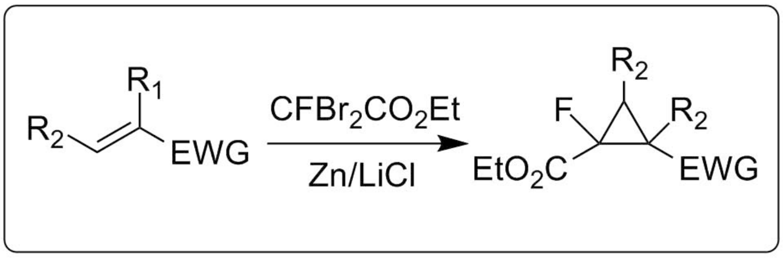
## A7.1

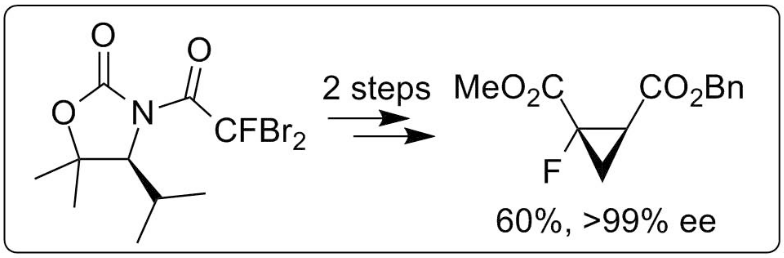
# Synthesis of highly functionalised monofluorinated cyclopropanes

**P. IVASHKIN** [(a)]* , **S. COUVE-BONNAIRE** [(a)], **P. JUBAULT** [(a)], **X. PANNECOUCKE** [(b)]

[(a)] INSA DE ROUEN, UMR 6014 COBRA - MONT SAINT-AIGNAN (FRANCE)
[(b)] IRCOF - INSA de Rouen, UMR 6014 COBRA - MONT SAINT-AIGNAN (FRANCE)

* pavel.ivashkin@insa-rouen.fr





Cyclopropane ring is the core structural motif of numerous biologically active compounds [1]. Moreover, the cyclopropanes are extensively used in the synthesis of diverse chemical products thanks to their unique reactivity based on the ring strain [2].

Partial fluorination of the cyclopropane ring has already been used to improve the biological activity and bioavailability of the pharmacologically active compounds [3]. However, synthetic and biological potential of fluorinated cyclopropanes has not been fully disclosed yet, partly because of the scarcity of the synthetic approaches to this class of compounds.

Here we report a new method for the synthesis of monofluorinated cyclopropanes from a wide range of electron-deficient alkenes (fig. 1) [4]. This cyclopropanation reaction proceeds via Michael-initiated ring closure and leads to the highly functionalised fluorinated cyclopropylcarboxylates. An asymmetric version of this cyclopropanation reaction was developed based on the use of a chiral fluorinated cyclopropanating reagent [5].

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[1] J. Salaun. *Top. Curr. Chem*, **207** (2000), 1.
[2] P. Tang, Y. Qin. *Synthesis*, **44** (2012), 2969.
[3] a) S. Hruschka *et al. Bioorg. Med. Chem.* **16** (2008), 7148. b) I. Ojima (Ed), Fluorine in medicinal chemistry and chemical biology; Wiley-Blackwell (2009).
[4] P. Ivashkin, S. Couve-Bonnaire, P. Jubault, X. Pannecoucke. *Org. Lett.* **14** (2012), 2270.
[5] P. Ivashkin, S. Couve-Bonnaire, P. Jubault, X. Pannecoucke. *Org. Lett.* **14** (2012), 5130.

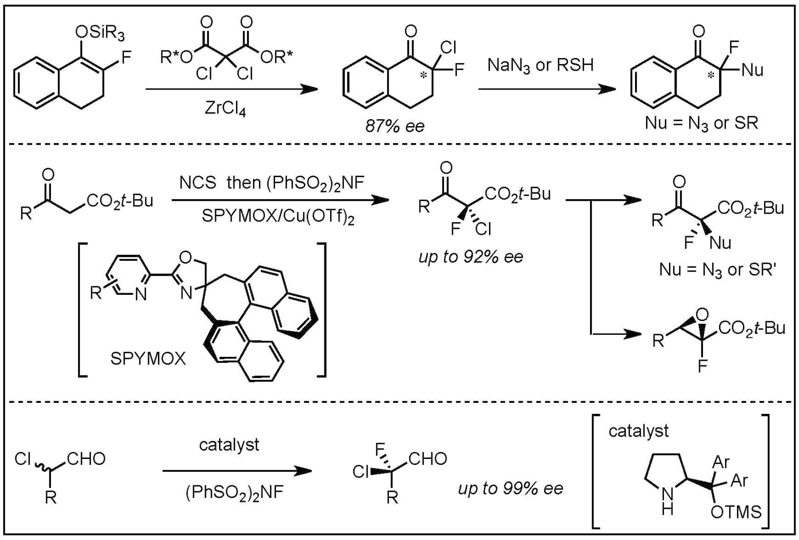
## A7.2

# Enantioselective Construction of Fluorinated Chiral Carbon Centers

**K. SHIBATOMI** [(a)] *

[(a)] TOYOHASHI UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF ENVIRONMENTAL AND LIFE SCIENCES - TOYOHASHI (JAPAN)

* shiba@ens.tut.ac.jp



The stereoselective synthesis of fluorinated organic molecules, especially the enantioselective construction of a fluorinated chiral carbon center, is a highly important subject in synthetic organic chemistry as well as in bio-organic chemistry.

We proposed the synthesis of optically active a-chloro-a-fluoro carbonyl compounds, which could be converted by nucleophilic substitutions into various chiral molecules with a fluorinated quaternary stereogenic center. Initially, optically active a-chloro-a-fluoro ketones were synthesized by the zirconium(IV) mediated asymmetric chlorination of a-fluorinated silyl enolates with chiral a,a-dichloromalonates as chlorination reagent.[1] Next, we synthesized chlorofluoro compounds with a new chiral Lewis acid catalyst which consists of copper(II) triflate and spiro chiral oxazoline ligand (SPYMOX). Sequential chlorination-fluorination of b-keto esters in the presence of Cu(II)/SPYMOX complex yielded the corresponding a-chloro-a-fluoro-b-keto esters in high enantioselectivity.[2] Enantioselective fluorination of racemic a-chloroaldehydes was also performed with a proline-derived chiral amine catalyst. The reaction successfully yielded desired a-chloro-a-fluoro aldehydes with up to 99% ee. These chlorofluoro compounds were converted into several fluorinated molecules by the nucleophilic substitution of a chlorine atom without loss of their enantiopurity.

We also succeeded in the enantioselective chlorination of a-alkyl-b-keto esters with Cu(II)/SPYMOX catalyst. Nucleophilic substitution of resulting a-chloro-b-keto esters with CsF proceeded in a stereospecific manner to afford the corresponding a-fluoro- b -keto esters.[3]

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## A7.3

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# Direct aldol-reduction process using difluoromethyl aryl ketones and aryl aldehydes in the presence of potassium *tert*-butoxide: one-pot efficient stereoselective synthesis of symmetrical and unsymmetrical *anti*-2,2-difluoropropane-1,3 diols

**W. XU [(a)], W. MURAMATSU [(b)(c)], M. BELLANCE [(b)], G. PILET [(d)], W. DOLBIER JR [(a)], M. MÉDEBIELLE [(b)*]**

[(a)] University of Florida, Department of Chemistry - GAINESVILLE (USA)
[(b)] Université Claude Bernard Lyon 1 (UCBL), Institut de Chimie et Biochimie Moléculaire et Supramoléculaire (ICBMS), UMR CNRS – UCBL, INSA Lyon 5246, Equipe « Synthèse de Molécules d'Intérêt Thérapeutique (SMITH) » - VILLEURBANNE (FRANCE)
[(c)] Nagasaki University, Graduate School of Biomedical Sciences - NAGASAKY (JAPAN)
[(d)] Université Claude Bernard de Lyon 1 (UCBL), Laboratoire des Multimatériaux et Interfaces (LMI), UMR CNRS – UCBL 5615 - VILLEURBANNE (FRANCE)

* maurice.medebielle@univ-lyon1.fr

2,2-difluoropropane-1,3-diols are a class of compounds of synthetic interest since they can be used, for example, as potential ligands in useful catalyzed transformations. Methods to prepare such diols in enantiopure forms are limited. We will disclose a new stereoselective and mild access to *anti* -2,2-difluoropropane-1,3-diols using readily available difluoromethyl aryl ketones and aryl aldehydes in the presence of potassium *tert*-butoxide.

Both symmetrical and unsymmetrical diols can be obtained in moderate to good yields through a possible aldol-Tischenko mechanism (Figure 1).

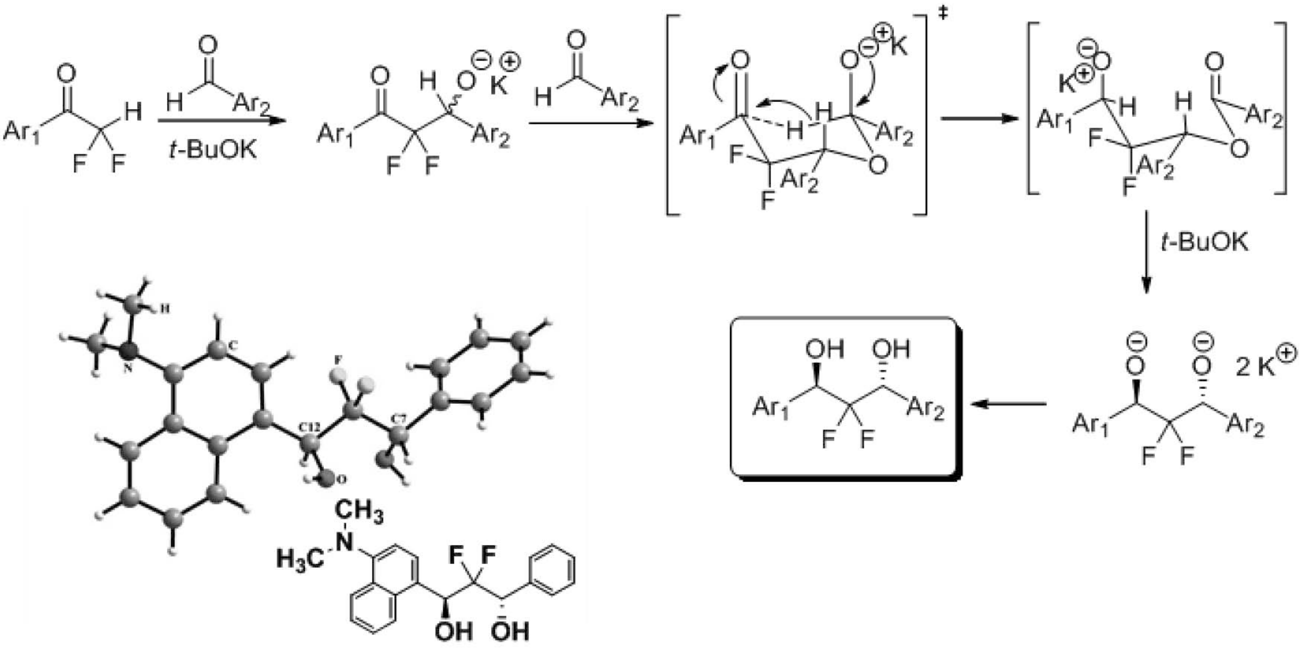

*Figure 1: New anti-2,2-difluoropropane-1,3-diols*

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## IL-A8

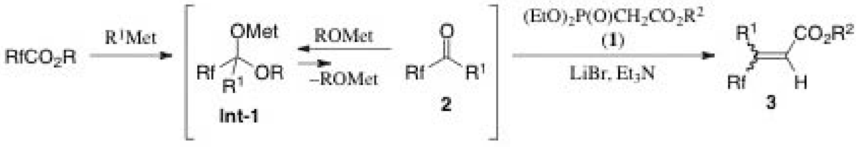
# Convenisent Stereoselective Synthesis of β-Perfluoroalkyl-β-alkyl α,β-Unsaturated Esters

**T. YAMAZAKI** [(a)]*

[(a)] TOKYO UNIVERSITY OF AGRICULTURE AND TECHNOLOGY, INSTITUTE OF ENGINEERING, DIVISION OF APPLIED CHEMISTRY - KOGANAI (JAPAN)

* tyamazak@cc.tuat.ac.jp

On the basis of the work by Burton *et al.* for the condensation of triethyl 2-fluorophosphonoacetate and *in situ* generated aldehydes from the corresponding esters by DIBAL reduction, we have devised a new route to get convenient access to β-Rf-β-R-substituted α,β-unsaturated esters in a stereoselective fashion using $RfCO_2R'$ as substrates. Thus, the intermediates Int-1 (Met: metals) after reaction of appropriate alkylmetals with $RfCO_2R'$ is considered to be in equilibrium with ketones 2 in preference to the former, and our desired materials 3 were eventually obtained by capture of 2 with Horner-Wadsworth-Emmons (HWE) reagents activated by combination of such safe chemicals as LiBr and $Et_3N$.



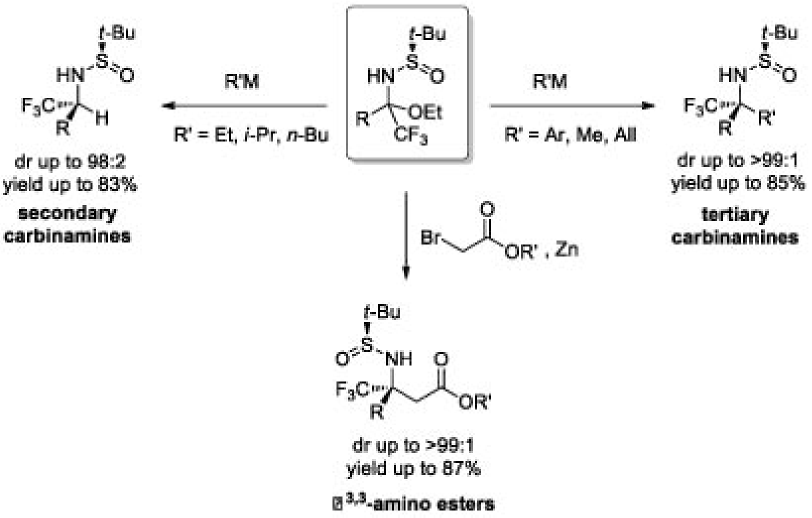
## A8.1

# Reactions of chiral alkyl and aryl trifluoromethyl N-*tert*-butanesulfinylhemiaminals with organometallic reagents

**F. GRELLEPOIS** [(a)*]

[(a)] UNIVERSITÉ DE REIMS-CHAMPAGNE-ARDENNE, ICMR UMR CNRS 7312 - REIMS CEDEX 2 (FRANCE)

* fabienne.grellepois@univ-reims.fr



Since its first report 15 years ago, chiral *N-tert*-butanesulfinamides developped by Ellman have been increasingly used for the preparation of a wide range of chiral mono- and poly-functionalized amines derivatives.[1] In spite of the obvious interesting properties of Ellman's chiral auxiliary such as the availability of both enantiomers and the mild conditions required for its cleavage, only a few publications deal with the applications of trifluoromethyl-substituted *N-tert*-butanesulfinyl ketoimines.[2] The presence of the activating substituent on the nitrogen atom makes the aliphatic and aromatic trifluoromethyl *N-tert*-butanesulfinyl ketoimines significantly more electrophilic than their *N*-alkyl or *N*-aryl analogues. They have to be generated and isolated quickly prior to use since they are unstable at room temperature and easily hydrolyzed or decomposed during work-up or purification on silica gel.

As the low hydrostability of aliphatic and aromatic trifluoromethyl *N-tert*-butanesulfinyl ketoimines significantly diminishs their potential synthetic value, we have recently reported the synthesis of the corresponding hemiaminals as bench stable surrogates.[3] Reaction of these chiral hemiaminals with organomagnesium or organolithium reagents provided secondary or tertiary carbinamines while the addition of Reformatsky reagent provided $\beta$-alkyl(aryl) $\beta$-trifluoromethyl $\beta$-amino esters derivatives.

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[3] F. Grellepois, *J. Org. Chem.* **78** (2013) 1127-1137.

## A8.2

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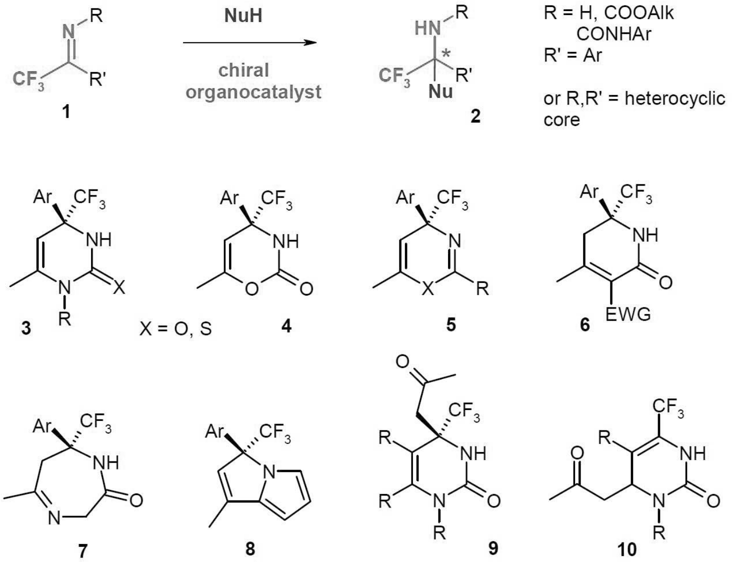
# Asymmetric organocatalytic synthesis of chiral trifluoromethylated heterocycles

**V. SUKACH** [(a)]*, **V. TKACHUK** [(a)], **V. SHOBA** [(a)], **M. VOVK** [(a)]

[(a)] Institute of organic chemistry, NAS of Ukraine - KYIV (UKRAINE)

* vsukach@bigmir.net

Asymmetric organocatalysis is a powerful tool for construction of optically pure synthetic blocks and complex molecular skeletons in modern stereoselective synthesis. One of the most important trends in this field is development of enantioselective approaches to fluoroalkyl substituted compounds bearing a chiral alpha-carbon center attached to a nitrogen atom. Asymmetric reactions of fluoroalkyl imines catalyzed with small organic molecules are of high usability for obtaining pharmacologically promising optically pure alpha-fluoroalkyl amines and their derivatives including heterocyclic compounds.



Asymmetric reactions of various acyclic trifluoromethyl ketimines of general structure (1) with C-nucleophiles in the presence of chiral organocatalysts have been studied. Enantiomerically enriched products (2) have been used as chiral building blocks for preparing of trifluoromethylated heterocyclic compounds (3-8) with endocyclic quaternary chiral center.

Applied strategy has allowed developing of direct asymmetric approaches to a diverse set of chiral functionalized
pyrimidines (9, 10) starting from heterocyclic trifluoromethyl ketimines 1.

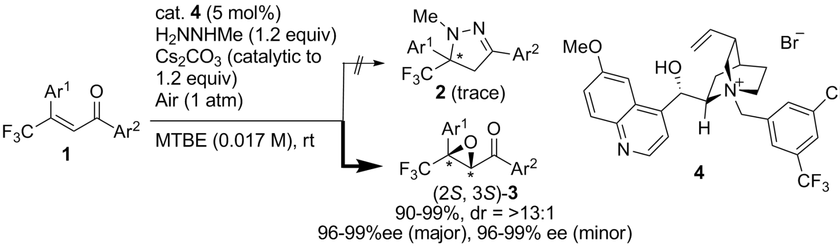
## A8.3

# Enantioselective Synthesis of Epoxides Having a Tetrasubstituted Trifluoromethylated Carbon Center: Methylhydrazine-Induced Aerobic Epoxidation of beta,beta-Disubstituted Enones

**N. SHIBATA** [(a)]*

[(a)] NAGOYA INSTITUTE OF TECHNOLOGY, DEPARTMENT OF FRONTIER MATERIALS - NAGOYA (JAPAN)

* nozshiba@nitech.ac.jp



| $Ar^1$ | $Ar^2$ | yield (%) | dr | ee [maj., min.] (%) |
|---|---|---|---|---|
| Ph | Ph | 91 | 95:5 | 99, 98 |
| 4-$MeC_6H_4$ | Ph | 92 | 94:6 | 99, 98 |
| 4-$ClC_6H_4$ | Ph | 90 | 95:5 | 98, 99 |
| Ph | 4-$MeC_6H_4$ | 91 | 93:7 | 98, 98 |
| Ph | 4-$ClC_6H_4$ | 92 | 93:7 | 98, 99 |

Ever since the asymmetric epoxidation of allylic alcohols milestone in the early 1980s by Sharpless,[1] the catalytic asymmetric epoxidation of olefins has become one of the most powerful, well-explored and very reliable transformations in organic synthesis to provide enantiomerically enriched epoxides, which are versatile building blocks for the synthesis of biologically active molecules and advanced materials. A large number of catalytic systems for asymmetric epoxidation have been devised over three decades and can be categorized into three classes according to the combination of catalysts and oxidants [2]: a) metal complex/active oxidant, b) metal complex/molecular oxygen, and c) organocatalyst/active oxidant. We disclose herein the first asymmetric epoxidation of beta,beta-disubstituted enones 1 having a beta-trifluoromethyl group by serendipitous discovery of a non-metallic, aerobic organocatalytic system consisting of methylhydrazine (H2NNHMe), base and a phase transfer catalyst from cinchona alkaloids 4. Enantiomerically enriched trifluoromethylated epoxides with a tetrasubstituted carbon center 3 were obtained for the first time, instead of pyrazolines 2, in excellent yields, excellent diastereoselectivity and enantioselectivities (96-99% ee).[3]

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## IL-A9

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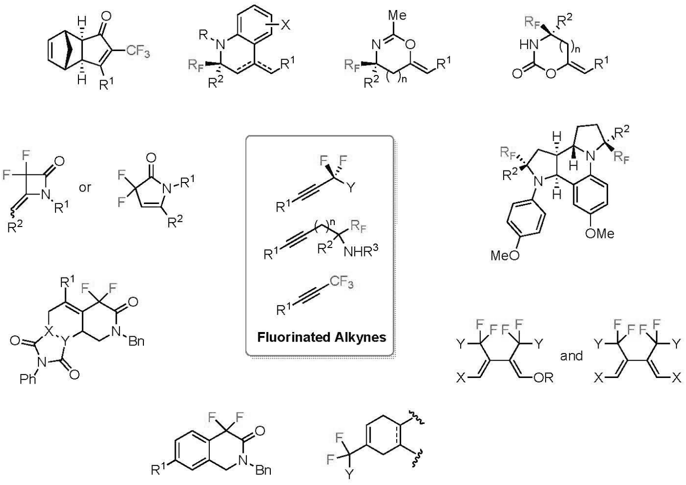
# New Transformations of Fluorinated Alkynes Mediated by Transition Metals

**C. DEL POZO** [(a)]*, **S. FUSTERO** [(a)]

[(a)] UNIVERSITY OF VALENCIA, DPTO. Q. ORGÁNICA - BURJASSOT (SPAIN)

* carlos.pozo@uv.es

Fluorinated organic compounds, in particular those containing nitrogen atoms, are popular targets in medicinal chemistry. In our laboratory, we were immersed on the development of new methodologies for the synthesis of new fluorinated carbo- and heterocycles for more than one decade. The transition-metal-mediated synthesis of fluorinated compounds has recently resulted in a renaissance of organometallic fluorine chemistry. In this context, we have explored the new perspectives offered by transition-metal catalyzed cyclization reactions of suitable fluorinated compounds containing unsaturated building blocks. In this communication I summarize recent methodologies for the synthesis of new nitrogen containing organofluorine compounds using fluorinated alkynes as starting substrates in their reactions with Pd, Rh, Ru, Au and Co complexes.



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[1] (a) S. Fustero, B. Fernández, P. Bello, C. del Pozo, S. Arimitsu, G. B. Hammond, *Org. Lett.*, **9** (2007) 4251. (b) S. Arimitsu, B. Fernández, C. del Pozo, S. Fustero, G. B. Hammond, *J. Org. Chem.*, **73** (2008) 2656. (c) S. Fustero, P. Bello, B. Fernández, C. del Pozo, G. B. Hammond, *J. Org. Chem.*, **74** (2009) 7690. (d) S. Fustero, P. Bello, J. Miro, A. Simón-Fuentes, C. del Pozo, *Chem. Eur. J.*, **18** (2012) 10991. (e) S. Fustero, P. Bello, J. Miró, M. Sánchez-Roselló, M. A. Maestro, J. González, C. del Pozo, *Chem. Commun.*, **49** (2013) 1336. (f) N. Aiguabella, C. del Pozo, X. Verdaguer, S. Fustero, A. Riera, Angew. Chem. Int. Ed., **52** (2013) early view.

## A9.1

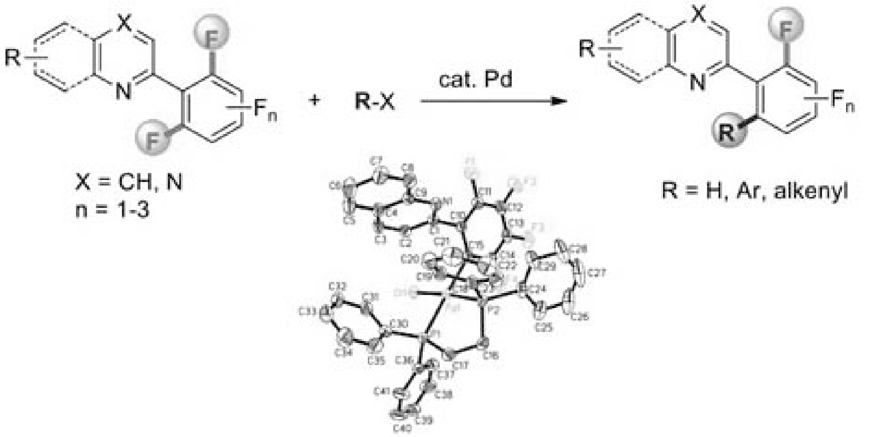
# Pd-Catalyzed *Ortho*-Selective C-F Activation of Polyfluroarenes

**Z. CHEN** [(a)], **C. HE** [(a)], **X. ZHANG** [(a)*]

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)

* xgzhang@mail.sioc.ac.cn

Owing to the unique characteristics of fluorine that often lead to profound changes in physical, chemical, and biological properties of organic molecules, partially fluorinated aromatics play an important role in life and materials sciences.[1] However, it is difficult to access these fluorinated compounds due to synthetic difficultiesand limited commercial availability of fluoroaromatic sources. One attractive approach to partially fluorinated aromatics is selective substitution of polyfluoroarenes through C-F bond activation, as polyfluoroarenes are more readily available and cheaper than their mixed halo or organometal counterparts. In the past few years, important progress has been made in this field.[2] However, the transition-metal-catalyzed *chemo*- and *regio*-selective transformations of C-F bonds remain a challenge due to the robustness of the C-F bond and difficulty in adjusting reaction selectivity of different C-F bonds on an aromatic ring.[3]On the other hand, azine/diazine (e.g., pyridine, quinoline, quinoxaline) substituted fluorinated aromatics bearing a hydride *ortho* to the heteroaryl groupare an important structural motif in light-emitting devices and photocatalysts. However, the limited synthetic methods and commercial availability of fluoroaryl patterns significantly limits the structural and functional diversity of this structural motif in further applications. As a continuous study in Pd-catalyzed polyfluoroarene chemistry,[4] herein, we describe our preliminary results on Pd-catalyzed *ortho*-selective C-F bond activation of polyfluoroarenes.[5]



*Pd-Catalyzed Ortho-Selective C-F Activation of Polyfluroarenes*

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## A9.2

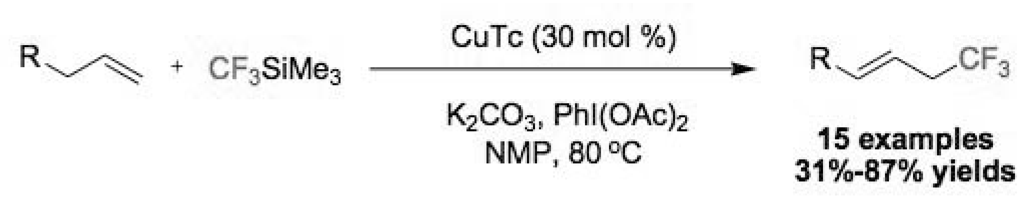
# Oxidative Trifluoromethylation of Unactivated Olefins with $CF_3SiMe_3$

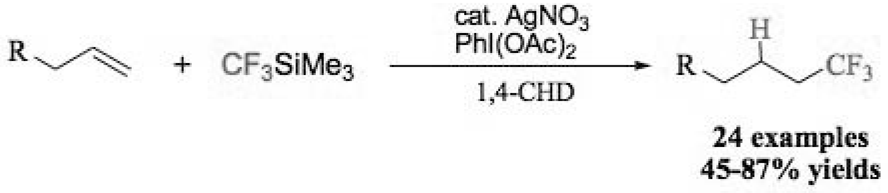
**F.L. QING** [(a)]*

[(a)] SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, KEY LABORATORY OF ORGANOFLUORINE CHEMISTRY - SHANGHAI (CHINA)

* flq@mail.sioc.ac.cn

Due to to the strong electron-withdrawing nature of the trifluoromethyl group (-$CF_3$), the incorporation of a trifluoromethyl group into organic molecules can dramatically modify a variety of properties, including lipophilicity, metabolic stability, and bioavailability. Notably, many billion-dollar pharmaceuticals as well as agrochemicals contain a trifluoromethyl group. Therefore, intensive attention has been recently attracted to the development of new methods for the introduction of the trifluoromethyl group into organic compounds.In contrast to the significant achievements that have been made in the trifluoromethylation of aromatic compounds, the trifluoromethylation of alkenes, especially unactivated alkenes, is still underdeveloped. Very recently, our group has developed the transition-metal catalyzed trifluoromethylation of unactivated alkenes with nucleophilic $CF_3Si(CH_3)_3$. In this talk, the copper-catylyzed oxidative trifluoromethylation of terminal alkenes and silver-catalyzed hydrotrifluoromethylation of unactivated olefins will be presented.





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## A9.3

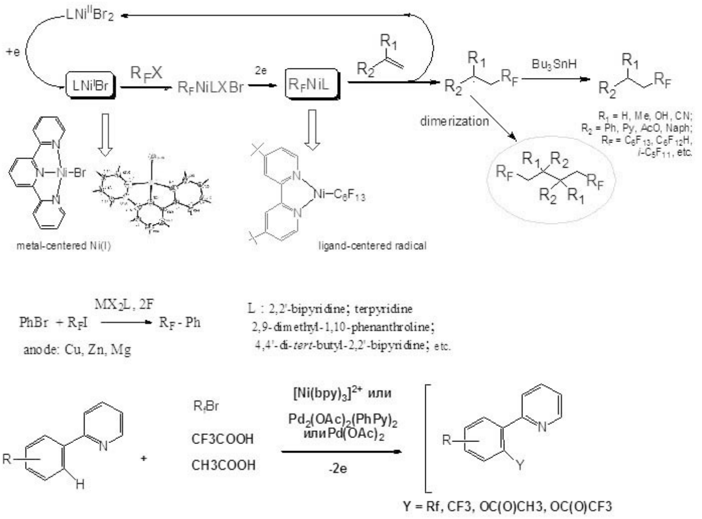
# Prospects of Synthetic Electrochemistry in the Development of New Methods of Electrocatalytic Fluoroalkylation

**Y. BUDNIKOVA** [(a)]*, **D. VICIC** [(b)], **Y. DUDKINA** [(a)], **D. MIKHAILOV** [(a)], **M. KHRIZANFOROV** [(a)], **T. GRYAZNOVA** [(a)]

[(a)] A.E.Arbuzov Institute of Organic and Physical Chem, ELECTROCHEMICAL SYNTHESIS LAB. - KAZAN (RUSSIAN FEDERATION)
[(b)] LEHIGH UNIVERSITY, DEPARTMENT OF CHEMISTRY - BETHLEHEM (USA)

* yulia@iopc.ru

Electrocatalytic generation of Ni catalysts in low oxidation states by reduction of Ni complexes with various α-diimine ligands (bipy, terpy, pybox) in the presence of olefinic substrates and fluoroalkyl halides leads to new products derived from addition-dimerization processes. The monomer formation proceeds in the presence of tributyltin hydride. Ni(I)L is the active form of the catalyst.



A one-step catalytic method for aromatic perfluoroalkylation with metal complexes electrochemical reduction under mild conditions with decisive role of the sacrificial anode metal ion has been developed. Cross-coupling is successful with bromo(iodo)benzene and perfluoroalkyl iodide and number of Co and Ni complexes.

Convenient approach to C-H substitution products based on electrochemical generation of Pd or Ni in high oxidation states is provided, and changing the number of the missing electricity can yield either ortho-acetoxylation and fluoracetoxylation product, or ortho-fluoroalkylation one. Fluorinated substituent in acid residues trouble somewhat the oxidation of dimeric palladium cycles compared to non-fluorinated compound. Record of EPR spectra during the oxidation of the dimer $Pd_2(PhPy)_2(OAc)_2$ allowed to fix the intermediate Pd (III).

## IL-A10

# Fluorination in superacid HF/SbF$_5$

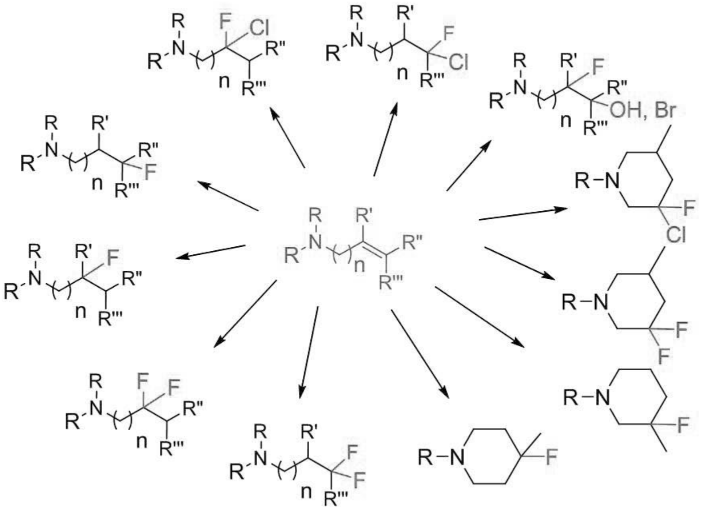
**S. THIBAUDEAU** [(a)]*

[(a)] Superacid group - Organic Synthesis team - UMR 7285 IC2MP - POITIERS (FRANCE)

* sebastien.thibaudeau@univ-poitiers.fr

Fluorinated analogues of nitrogen containing biologically active compounds are regarded as tools of relevant interest for pharmaceutical research. Consequently the discovery of new methods to access fluoroamines remains a major challenge in synthetic chemistry. Based on superelectrophilic activation,[1] a range of unsaturated amines and sulfonamides can be converted to fluorinated analogues *via* novel reactions in superacid HF/SbF$_5$.[2]

Some of the synthesized fluorinated derivatives show biological activities.[3] This work opens new possibilities for the direct and effective preparation of fluorinated nitrogen compounds of high synthetic and biological values.



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## A10.1

# Hydrogen-Bond Donation Promotes C-F Bond Activation for Nucleophilic Substitutions on Activated Alkyl Fluorides

**P.A. CHAMPAGNE** [(a)*], **Y. BENHASSINE** [(a)], **J. PAQUIN** [(a)]

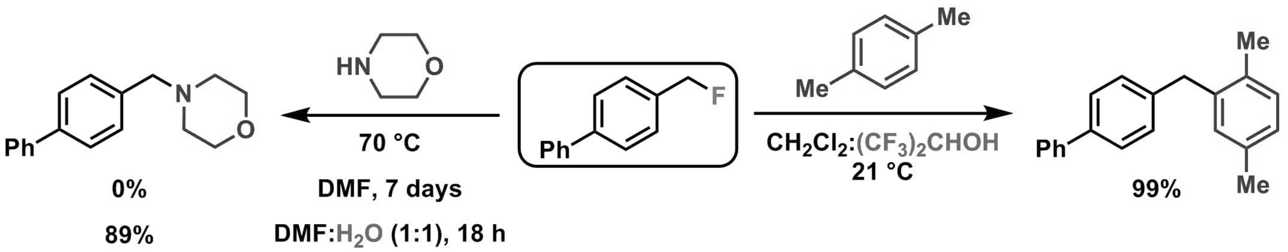
[(a)] Université Laval - QUEBEC CITY (CANADA)

* pier-alexandre.champagne.1@ulaval.ca

Simple alkyl fluorides are generally regarded as poor electrophiles in nucleophilic substitution reactions, mainly because of the strength of the carbon-fluorine bond. Only a few examples of such transformations have been described, all under strictly basic conditions; however alkyl fluorides are somewhat reactive under strongly acidic conditions or in the presence of transition metals.[1]

Herein, we document the nucleophilic substitution reaction of activated alkyl fluorides almost under neutral conditions. The scope of the reaction includes the use of *N*-, *O*-, *S*- and *C*-nucleophiles with various activated alkyl fluorides. Experimental evidences and DFT calculations suggest that hydrogen-bond donation from the solvents plays a crucial role in the observed reactivity, by activating the C-F bond and stabilizing the exiting fluoride ion.[2]

In addition, the use of stronger hydrogen-bond donors modifies the reaction pathway and enables the use of benzylic fluorides in Friedel-Crafts reactions. Optimization of the conditions, scope of the reaction and preliminary mechanistic studies for this transformation will also be presented.[3]



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[3] Benhassine, Y.; Champagne, P. A.; Paquin, J.-F. *In preparation*.

## A10.2

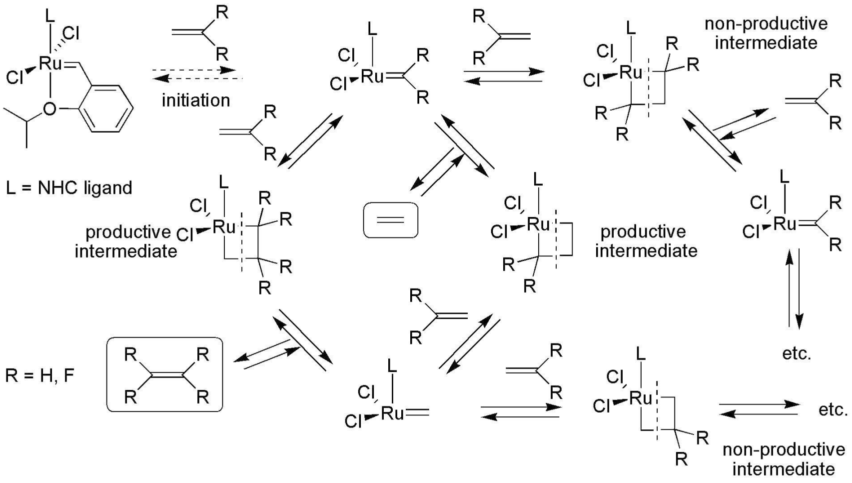
# DFT Study on Fluoroalkene Metathesis: The Role of Productive and Non-productive Cycles

**J. KVICALA** [(a)]* , **M. RYBACKOVA** [(a)], **J. HOSEK** [(a)], **O. SIMUNEK** [(a)]

[(a)] Department of Organic Chemistry, INSTITUTE OF CHEMICAL TECHNOLOGY, PRAGUE - PRAGUE 6 (CZECH REPUBLIC)

* jaroslav.kvicala@vscht.cz

Information regarding metathesis of alkenes bearing fluorine on the double bond is severely limited. Thus, Grubbs 2nd generation catalyst reacts with vinylidene fluoride to stable non-reactive difluoromethylene complex [1], while analogous monofluorinated catalyst displayed limited activity in RCM [2]. Haufe et al. showed that the success of fluoroalkene metathesis often depends on minor variations in fluoroalkene backbone [3].



We hence started a DFT study of the metathesis of model fluoroalkenes with the aim to understand the role of the stability of individual reaction intermediates, as well as transition states, and thus to gain insight into the participation of productive and non-productive catalytic cycles (Fig. 1). Calculations confirmed high stability of fluoromethylene complexes observed experimentally, but also disclosed dominant position of the non-productive cycles including 2- and 4-fluoro substituted ruthenacyclobutanes.

*We thank the Grant Agency of the Czech Republic for financial support (grant No. 207/10/1533).*

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## A10.3

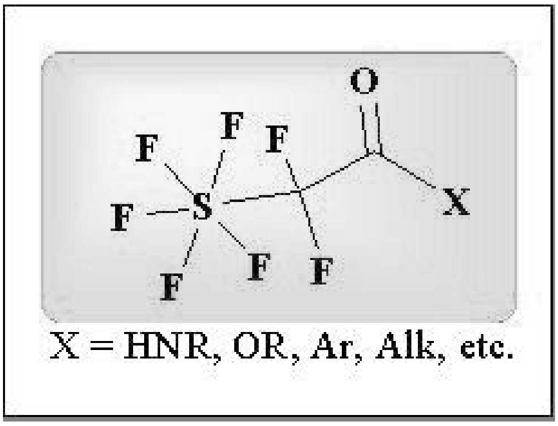
# Synthesis and applications of pentafluorosulfanyldifluoroacetic acid

**A.V. MATSNEV** [(a)]* , **M.A. STANTON** [(a)], **S. QING** [(a)], **G. HAUFE** [(b)], **J.S. THRASHER** [(a)]

[(a)] Department of Chemistry, Clemson University, Advanced Materials Research Laboratory - ANDERSON, SC (USA)
[(b)] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)

* a.v.matsnev@gmail.com

Compounds with a pentafluorosulfanyl ($SF_5$) group have been attracting great interest over the last six decades since the first organic $SF_5$-containing molecules were synthesized. The pentafluorosulfanyl group brings unique properties to organic compounds and often improves their biological activities because of the group`s high chemical and metabolic stability, significant lipophilicity, substantial steric effect and low surface energy [1].



However, for the most part, the development of $SF_5$ chemistry has been quite slow primarily due to the lack of pentafluorosulfanyl-containing building blocks and/or useful synthetic methods for their preparation.

For example, one of the most interesting reagents could be pentafluorosulfanyldifluoroacetic acid ($SF_5CF_2$ C(O)OH) [2], but all of the known methods for its preparation either were unsafe or produced the acid in extremely low yield.

Recently, we have been able to develop several convenient methods for the synthesis of the $SF_5CF_2$ C(O)OH. In the present work, we will discuss the scopes and limitations of these methods as well as applications of the pentafluorosulfanyldifluoroacetic acid in the synthesis of potentially valuable compounds.

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## A10.4

# Synthesis and Catalysis of Fluorinated Organic Brønsted Acids

**H. YANAI** [(a)]*, **T. YOSHINO** [(a)], **N. ISHII** [(a)], **T. TAGUCHI** [(a)]

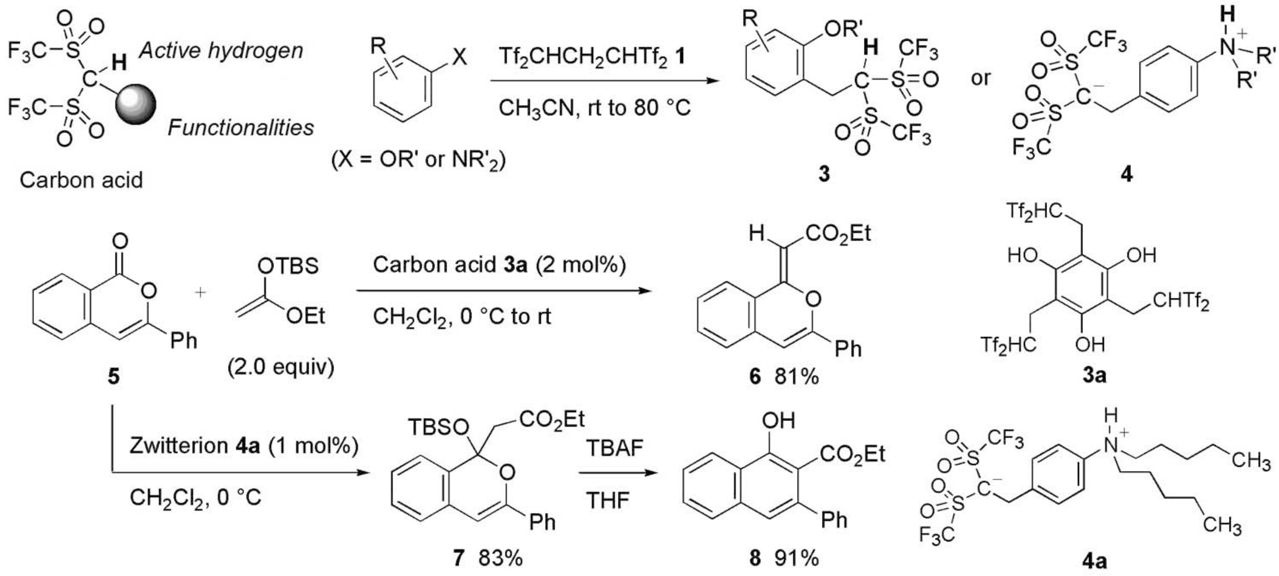
[(a)] TOKYO UNIVERSITY OF PHARMACY AND LIFE SCIENCES, SCHOOL OF PHARMACY - TOKYO (JAPAN)

* yanai@toyaku.ac.jp

Recently, our research is focusing on organic acids bearing gem-di(triflyl)methyl group as a key functionality. For example, we reported 1,1,3,3-tetrakis(triflyl)propane 1, $Tf_2CHCH_2CHTf_2$ ($Tf = CF_3SO_2$), as an excellent molecular catalyst for some synthetic reactions including the Mukaiyama aldol type reactions and the Mukaiyama–Michael reaction. In this Symposium, we would like to demonstrate a novel methodology to prepare the carbon acid derivatives and their catalysis.

On the basis of the in situ-generation of highly reactive $Tf_2C=CH_2$ 2 via retro Michael reaction of tetrasulfone 1, we examined the trapping of 2 with neutral nucleophiles. When electron-rich arenes such as phenols and aryl ethers were treated with tetrasulfone 1 in $CH_3CN$, clean formation of the corresponding adducts were achieved.[1a] Interestingly, we also obtained unique zwitterions by the reaction of anilines.[1b]

These acidic species showed notable catalyst performance in the reaction of lactones with silicon enolates. That is, in the presence of carbon acid 3a, the reaction of isochromenone 5 with a ketene silyl acetal gave unusual olefination product 6 in 81% yield.[2] On the other hand, the use of less acidic zwitterion 4a instead of 3a resulted in selective formation of adduct 7. This adduct easily converted to 1-naphthol 8 by treating with fluoride ion. Details will be presented.



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# STREAM B

## THURSDAY, JULY 25

## IL-B7

# Rare earth doped inorganic fluoride materials: synthesis and applications

**M. MORTIER** [(a)]*, **P. ABALLEA** [(a)], **H. SERRIER-BRAULT** [(a)], **T. DHEIVASIGAMANI** [(a)], **L. MICHELY** [(a)], **P. GREDIN** [(b)], **G. PATRIARCHE** [(c)]

(a) LCMCP, CNRS, Chimie ParisTech - PARIS (FRANCE)
(b) LCMCP, CNRS, UPMC - PARIS (FRANCE)
(c) LPN - CNRS - MARCOUSSIS (FRANCE)

* michel-mortier@chimie-paristech.fr

The proliferation of lasers and other opto-electronic technologies for telecommunication, remote sensing, materials processing, and defense has generated substantial interest in materials with exceptional optical properties. The precise nature of these desirable optical properties varies widely with the intended application and includes exceptionally low optical losses for long distance data transfer, wide transparency windows for multispectral imaging, and efficient energy transfer/storage for laser and frequency converters. Today, the vast majority of optical components are crystals or glasses composed of oxide materials, but there have been many sustained research efforts on fluorides where unique optical properties make them ideal candidates for specific optical applications.

Because of the highly ionic bond character, inorganic fluoride compounds have compelling advantages for many optical applications due to their unique combination of low phonon energy, high UV absorption edge energy, and relatively weak crystal field.

This property makes fluorides good candidates for laser, window, and lens applications in the ultraviolet (UV) and vacuum ultraviolet (VUV) wavelength range. When doped with rare earth ions, non-radiative de-excitation probabilities are weaker for fluorides than for oxides allowing particularly efficient emission in the infrared range where multiphonon processes increase non-radiative decay rates in many oxide laser hosts. Moreover, the weak crystal field in fluorides reduces the probabilities of cross-relaxation between luminescent active ions. Long excited state lifetimes in fluorides facilitate upconversion processes for blue and UV lasers.

Fluorides have seen adoption and study in the fields of single crystals, glasses, glass–ceramics, and transparent ceramics. In this presentation, we review the current state of the art in fluoride materials for optical applications. We will address the chemistry and properties of fluoride single crystals and glasses as well as the processing and properties of fluoride transparent ceramics for high power lasers.

## B7.1

# PROGRESS IN FLUORIDE LASER CERAMICS

**P. FEDOROV [a]* , M. DOROSHENKO [b], E. GARIBIN [c], V. OSIKO [a]**

[a] A.M. PROKHOROV GENERAL PHYSICS INSTITUTE RUSSIAN ACADEMY OF SCIENCES, LASER MATERIALS AND TECHNOLOGY RESEARCH CENTER - MOSCOW (RUSSIA)
[b] GPI RAS - MOSCOW (RUSSIA)
[c] INCROM Ltd. - ST. PETERSBURG (RUSSIA)

* ppfedorov@yandex.ru

The history of fluoride laser ceramics begins in 1964 [1], but it was the preparation of fluoride laser ceramics via the hot forming technique that provided a tremendous boost in this area of research and manufacturing. This method is based on the pressure deformation of the single crystals at higher temperatures [2-4]. Application of this technique made available lasing ceramic fluoride matrixes CaF$_2$, SrF$_2$, (Ca,Sr)F$_2$, (Sr,Ba)F$_2$ doped with Yb$^{3+}$, Nd$^{3+}$, Pr$^{3+}$, Tm$^{3+}$, and Er$^{3+}$ [2-9], including CaF$_2$:Yb ceramics (Fig.1). The latter samples possess spectral (including luminescent) and lasing properties similar to that of single crystals. At the same time, the use of an alternative classic technique of hot pressing of powder precursors resulted in significant improvement of the mechanical properties of prepared laser ceramics, while maintaining the same lasing, spectral and other qualities [8], such as thermal conductivity, thermal expansion, heat capacity, microstructure, etc. [4,9-11].

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## B7.2

# Novel Cationic Iridium Complexes for Blue Phosphorescent OLEDs

**Y. TAKAHIRA** [(a)]* **, E. MUROTANI** [(a)]**, K. FUKUDA** [(a)]

[(a)] ASAHI GLASS CO., LTD., RESEARCH CENTER - YOKOHAMA (JAPAN)

* yusuke-takahira@agc.com

Cyclometalated iridium (III) complexes are attractive materials in terms of their applications in organic light-emitting diodes (OLEDs) [1]. One of the critical issues among the related investigations is that few blue phosphorescent complexes reported so far exhibit sufficient color index and emission efficiency. For example, FIrpic, well-known as a *de facto* blue phosphor, has the CIEx,y coordinates of (0.16, 0.32) [1], whereas CIEx and CIEy are desired less than 0.2 as a ‘true-blue’ color for excellent color-rendering properties in the OLED display use.

Here, we demonstrate the synthesis of a series of cationic iridium complexes. Optimizing the structure of complexes, we have successfully developed a novel blue phosphor BD-141 [2]. Its CIEx,y coordinates was estimated to be (0.17, 0.18), which obviously indicated that this newly developed complex is a promising candidate for true-blue phosphorescent material. Notably, BD-141 exhibited excellent photoluminescent properties in a diluted solution and its photoluminescent quantum yield reached up to 83%. Moreover, BD-141 has good solubility in common organic solvents, which can enable thin-film fabrication by spin-coating method. Further studies for preparing the light-emitting devices will be also discussed.

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## B7.3

# Synthesis and luminescent characteristics of $NaYF_4$:Yb:Er powders for photodynamic cancer therapy.

**S. KUZNETSOV** [(a)]* , **D. YASIRKINA** [(b)], **N. RYABOVA** [(b)], **D. POMINOVA** [(b)], **P. FEDOROV** [(b)], **V. VORONOV** [(b)], **O. UVAROV** [(b)], **V. OSIKO** [(b)], **A. BARANCHIKOV** [(c)]

[(a)] A.M. PROKHOROV GENERAL PHYSICS INSTITUTE RUSSIAN ACADEMY OF SCIENCES, TECHNOLOGY OF NANOMATERIAL FOR PHOTONICS - MOSCOW (RUSSIA)
[(b)] A.M. PROKHOROV GENERAL PHYSICS INSTITUTE RUSSIAN ACADEMY OF SCIENCES, LASER MATERIALS AND TECHNOLOGY RESEARCH CENTER - MOSCOW (RUSSIA)
[(c)] KURNAKOV INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY OF RUSSIAN ACADEMY OF SCIENCES - MOSCOW (RUSSIA)

* kouznetzovsv@gmail.com

While studying the synthesis of $NaYF_4$:Yb:Er powder by co-precipitation from aqueous solutions, we have found that the following factors play crucial roles in the preparation of products of acceptable quality: (1) initial concentrations and ratios of starting material solutions, (2) the order of their mixing, (3) concentration of polyethyleneimine (PEI) additive, and (4) pH of the initial solutions. Namely, 25% excess of NaF is required for the preparation of single-phase samples, and preparation should be carried out by addition of metal nitrate solutions to 9 g/L PEI-doped 0.35 M aqueous NaF at pH = 10. According to scanning electron microscopy (SEM) data, this leads to the formation of 50-90 nm particles of cubic phase. The use of PEI concentration of 9 g/L resulted in the precipitation of 100-150 nm particle agglomerates (0.3-1 mm elongated agglomerates, SEM data) (hexagonal phase). Transmission electron microscopy (TEM) study of cubic $NaYF_4$:Yb:Er samples indicated that they consisted of several nm primary particles with 50 nm embryo agglomerates and 160 nm particle agglomerates. TEM data confirm the realization of the non-classical mechanism of crystal growth via the nanoparticle agglomeration. Powder samples of cubic $NaYF_4$:Yb:Er provided up to 2% luminescence quantum yield and can be used as working agent in photodynamic cancer therapy.

This work was supported by RFBR 12-02-00851-a (Russian Federation State Contract 14.740.12.1343). TEM measurements were carried at the Center of mutual use of equipment at Prokhorov General Physics Institute.

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## IL-B8

# New developments in synthetic and structural noble-gas chemistry; The Coordination Behaviors of $NgF_2$ (Ng = Kr, Xe) Towards Metal and Non-Metal Centers; and the Syntheses of $FXeOXO_3$ (X = Cl, Br) and Related $XO_2^+$ Complexes of $NgF_2$

**G.J. SCHROBILGEN [a]*, U. BREDDEMANN [a], J. HANER [a], D.S. BROCK [a], H.P.A. MERCIER [a], M. ELLWANGER [a], J.R. DeBACKERE [a], M. LOZINŠEK [b], B. ŽEMVA [b]**

[a] DEPARTMENT OF CHEMISTRY, McMaster University - HAMILTON (CANADA)
[b] Department of Inorganic Chemistry and Technology, Jožef Stefan Institute - LJUBLJANA (SLOVENIA)

* schrobil@mcmaster.ca

Both $KrF_2$ and $XeF_2$ have recently been shown to interact in anhydrous hydrogen fluoride (aHF) with Br(V) in $[BrOF_2][AsF_6]$ by means of fluorine bridges to form the coordination complexes, $[BrOF_2][AsF_6]{\bullet}2KrF_2$ and $[BrOF_2][AsF_6]{\bullet}2XeF_2$. The noble-gas difluorides have been previously shown by low-temperature $^{19}F$ and $^{129}Xe$ NMR and Raman spectroscopy to coordinate to Group 6 $d^o$-metal oxide tetrafluorides; e.g., $NgF_2{\bullet}MOF_4$ (Ng = Kr, Xe; M = Cr, Mo, W). The low-temperature crystal structures of $NgF_2{\bullet}MOF_4$, $NgF_2{\bullet}2MoOF_4$,$XeF_2{\bullet}2WOF_4$, and $NgF_2{\bullet}2CrOF_4$ have been obtained and will be discussed. The $Ng\square F_t$ and $M\square F_b$ bond length trends in the $NgF_2{\bullet}MOF_4$ series are consistent with the Lewis acidity order $CrOF_4 < MoOF_4 < WOF_4$ and with the fluoride ion donor strength order $KrF_2 < XeF_2$.

Xenon difluoride forms fluorine-bridged complexes in aHF with a large number of metal cations, e.g., $[Cd(XeF_2)][BF_4]_2$, $[Ca_2(XeF_2)_9][AsF_6]_4$, and $[Mg(XeF_2)_4][AsF_6]_2$. Neutral Hg(II)−$NgF_2$ coordination complexes with $Hg(OTeF_5)_2$ have been synthesized in $SO_2ClF$ solution and isolated. Thus far, the X-ray crystal structure of $(F_5TeO)_2Hg{\bullet}1.5XeF_2$ has been determined. Prior to this work, no examples in which $KrF_2$ functions as a ligand towards an alkaline earth metal cation or any other metal cation had been documented. In collaborative work with Boris Žemva and Matic Lozinšek (Jožef Stefan Institute, Ljubljana, Slovenia), the $[Mg(KrF_2)_4][AsF_6]_2{\bullet}2BrF_5$ complex has been synthesized in $BrF_5$ solvent and fully characterized by single-crystal X-ray diffraction. The coordination around $Mg^{2+}$ is analogous to that previously reported for $[Mg(XeF_2)_4][AsF_6]_2$.

The reactions of $NO_2F$ and $ClO_2F$ with $[FXeOXeFXeF][AsF_6]$ at low temperatures have yielded the first noble-gas nitrate, $FXeONO_2$, and, more recently, the perchlorate, $FXeOClO_3$. In the latter case, the $XeF_2$ coordination complex, $[ClO_2][AsF_6]{\bullet}2XeF_2$, is also formed. The reactivity of $ClO_2F$ with the $Xe_3OF_3^+$ cation demonstrates the ability of $Xe_3OF_3^+$ to function as an oxygen transfer reagent, oxidizing Cl(V) to Cl(VII). The analogous bromine chemistry will also be discussed.

## B8.1

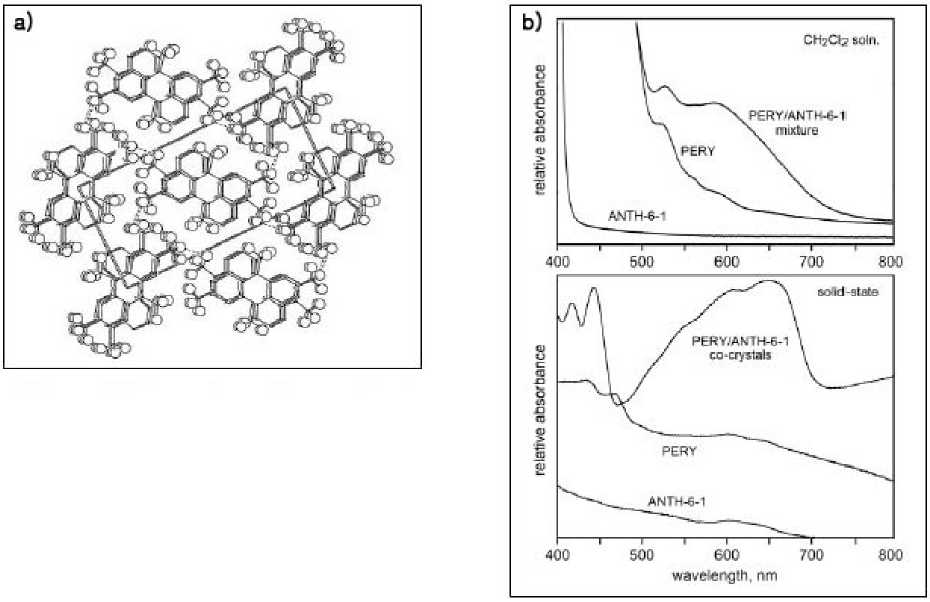
# Infinite Insulated Pi-Stacked Donor/Acceptor Molecular Arrays: –[PAH´/PAH(CF$_3$)$_n$]$_\infty$- Charge-Transfer Co-Crystals

**I.V. KUVYCHKO** (a), **K.P. CASTRO** (a), **E.V. BUKOVSKY** (a), **O. BOLTALINA** (a), **Y.S. CHEN** (b), **S.H. STRAUSS** (a)*

(a) DEPARTMENT OF CHEMISTRY, Colorado State University - FORT COLLINS (USA)
(b) ChemMatCARS Beamline, University of Chicago Advanced Photon Source - ARGONNE (USA)

* steven.strauss@colostate.edu

The X-ray crystal structures and solution/solid-state charge-transfer spectra of –[PAH'/PAH(CF$_3$)n]$_\infty$– donor/acceptor co-crystals for PAH or PAH' = anthracene (ANTH), azulene (AZUL), perylene (PERY), pyrene (PYRN), among others, and n = 4–6 will be presented and discussed (the abbreviation PAH(CF$_3$)$_n$ denotes n H atoms replaced by n CF$_3$ groups (e.g., ANTH(CF$_3$)$_6$ denotes C$_{14}$H$_4$(CF$_3$)$_6$, not C$_{14}$H$_{10}$(CF$_3$)$_6$)). The structures of several co-crystals exhibit parallel infinite stacks of alternating PAH' and PAH(CF$_3$)$_n$ molecules which are insulated from one another by CF$_3$ groups, as shown in Figure a) for PERY/ANTH-6-1. Several co-crystals consisting of colorless PAH and PAH(CF$_3$)$_n$ compounds are distinctly colored, evidence of solid-state charge transfer. For example, colorless ANTH and ANTH-6-1 form bright-orange 1:1 co-crystals. Furthermore, a mixture of these two compounds in dichloromethane solution is also orange, indicating the formation of charge-transfer complexes in solution as well as in the solid state. Figure 2 shows the charge transfer spectra in solution (1:1 mixture) and in the solid state (1:1 co-crystals) of PERY/ANTH-6-1.



*a) View down the a axis of PERY/ANTH-6-1 co-crystals. b) electronic spectra of PERY/ANTH-6-1 co-crystals.*

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## B8.2

# Complexes of Cyclic π-Perimeters with Perfluorinated Vinyl Side Chains

**D. HEINRICH** [(a)]* , **D. LENTZ** [(a)]

[(a)] FREIE UNIVERSITÄT BERLIN, Institut für Chemie und Biochemie - BERLIN (GERMANY)

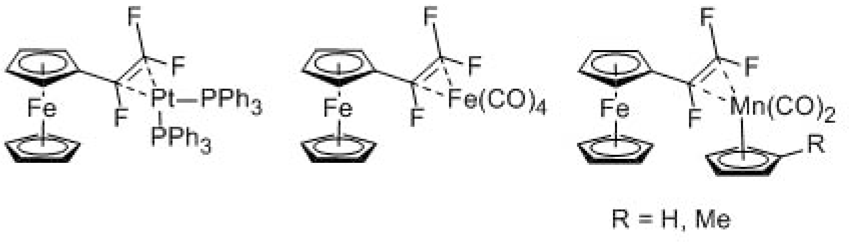
* dheinrich@zedat.fu-berlin.de

Trifluorovinyl groups offer the opportunity for many different types of reactions. Recently, we reported on the synthesis and rich chemistry of trifluorovinylferrocene derivatives, especially the nucleophilic substitution and [2+2]-cycloaddition reactions used for polymerization. [1,2]

Although fluoro-olefinic compounds are excellent π-acceptor ligands in coordination and organometallic chemistry, their transition metal chemistry is scarcely investigated in contrast to their hydrocarbon analogues. [3] Most known metal complexes are limited to simple fluorinated monoalkenes like tetrafluoroethene, may be due the different polymerization mechanism. While the reaction of hydrocarbon olefins contains a metal coordinating step, fluoropolymers are formed by free radical polymerization. Recently the increasing interest to activate the unreactive C-F bond refocused the fluoro-organometallic chemistry.

Herein we present the first complexes using trifluorovinylferrocene and 1,1'-bis(trifluorovinyl)ferrocene as ligands. They are obtained either by ligand substitution in ethylenebis(triphenylphosphine)platinum(0) and tricarbonyl-($\eta^5$-cyclopentadienyl)manganese or treatment with nonacarbonyldiiron by forming pentacarbonyliron as a side product (Fig. 1.). The crystal structure determinations show a loss of planarity of the alkene as a result of the coordination in accordance with the higher p-character of the hybrid orbitals.

Additionally, we studied the reactivity of the platinum species in presence of lithiumorganyls and Lewis acids like lithium iodide to initiate an oxidative addition by carbon-fluorine bond activation and subsequent lithium fluoride elimination.



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## B8.3

# «$XeF_2$ rich» and «$XeF_2$ poor» compounds in the system $XeF_2$ - $TiF_4$

**K. RADAN** [(a)]* , **E.A. GORESHNIK** [(a)], **B. ŽEMVA** [(a)]

[(a)] Jožef Stefan Institute, DEPARTMENT OF INORGANIC CHEMISTRY AND TECHNOLOGY - LJUBLJANA (SLOVENIA)

* kristian.radan@ijs.si

In order to clarify the true nature of the first noble gas compound "$XePtF_6$" isolated by Bartlett [1] in 1962, a variety of experiments using different synthetic approaches were carried out. These studies were later extended to other similar systems $XeF_2$ – $MF_4$ (M = Cr, Mn, Pd, Pt, Rh, Sn, Ti). Several compounds were synthesized, but only in four cases the crystal structures were obtained ($XeF_2 \bullet CrF_4$ [2], $XeF_2 \bullet 2CrF_4$ [3], $3XeF_2 \bullet 2MnF_4$ [4], $XeF_2 \bullet MnF_4$ [4]). The rich structural diversity of the above mentioned compounds provides a strong motivation for further research of these systems, which may lead to a better understanding of the interaction between a medium strong fluoride ion donor $XeF_2$ and some metal tetrafluorides acting as fluoride ion acceptors.

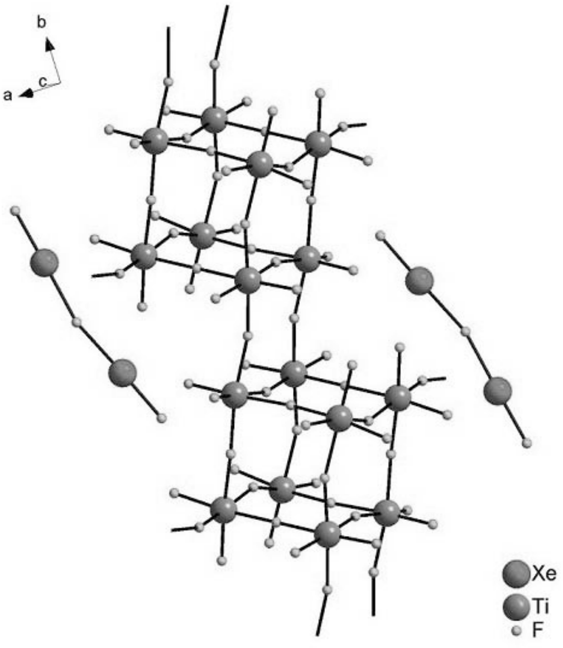

Fig. 1. X – ray crystal structure of $Xe_2F_3Ti_8F_{33}$.

Recently we focused our attention on the $XeF_2$ – $TiF_4$ system, where three novel compounds were isolated and structurally characterized: $3XeF_2 \bullet 2TiF_4$, $Xe_2F_3Ti_8F_{33}$ and $(XeF)_2Ti_9F_{38}$. The first compound crystallized from a solution of $TiF_4$ and excess $XeF_2$ in anhydrous HF and is isostructural with the known manganese analogue $3XeF_2 \bullet 2MnF_4$ [4]. In an attempt to prepare $XeF_2 \bullet 2TiF_4$, the compounds $Xe_2F_3Ti_8F_{33}$ and $(XeF)_2Ti_9F_{38}$ were isolated from the solid reaction mixture of $XeF_2$ and $TiF_4$ in a 1:2 molar ratio. The mixture was heated to 135 °C and the crystallization was achieved by careful cooling of the melt to room temperature. The formation of a $Xe_2F_3^+$ salt under such conditions is somewhat unexpected and represents the first compound with the aforementioned cation in the systems $XeF_2$ – $MF_4$. Most probably, the salt $(XeF)_2Ti_9F_{38}$ with the novel nonameric polyanion $(Ti_9F_{38}^{2-})_n$ forms from the $Xe_2F_3Ti_8F_{33}$ compound reacting with an additional $TiF_4$ at elevated temperatures. The Raman spectrum of $(XeF)_2Ti_9F_{38}$ additionally confirms a high degree of $XeF_2$ ionization, suggesting the formation of a $XeF^+$ compound.

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## IL-B9

# Recent advances in developing new low GWP alternatives to Hydrofluorocarbons and hydrochlorofluorocarbons

**M. NAPPA** [(a)]*

[(a)] E. I. DUPONT DE NEMOURS AND CO., EXPERIMENTAL STATION E262/325 - WILMINGTON (USA)

* mario.j.nappa@usa.dupont.com

F-Gas regulations adopted in Europe call for the elimination of high global warming potential automobile refrigerants (GWP >150) in “new type” vehicles beginning in 2011, and in “all new vehicles” beginning in 2017. This mandate is similar to what the chemical industry experienced with the Montreal Protocol and the reduction of CFCs for their high ozone depletion potential nearly two decades ago. This regulation has been a stimulus for the chemical industry to look for low global warming alternatives for all of its fluorochemical offerings. The need for the automobile industry to switch refrigerants has led DuPont and others to search for new low GWP environmentally acceptable offerings to replace HFC-134a ($CF_3CH_2F$) which has been in service since the early 90’s. This presentation will focus on the recent developments of these new types of molecules for a variety of markets such as refrigerants, foam expansion agents, fire extinguishants, solvents and other high performance fluids.

## B9.1

# Environmental Chemistry of Ultra-low GWP Fluorocarbons

**R. SINGH** [(a)]*

[(a)] HONEYWELL INTERNATIONAL, FLUORINE PRODUCTS - BUFFALO (USA)

* Rajiv.Singh@Honeywell.com

We present environmental chemistry of new GWP fluorocarbon molecules that are being commercialized for large applications, such as aerosols, refrigeration and blowing agents, that can be used in existing Fluorocarbon equipment with little or no system redesign. They have GWP(100) values of 6 and 7 Respectively. Since the traditional fluorocarbons have been implicated in Ozone depletion and/or Climate Change, it is very important that any other environmental problems do not arise with the new class of low GWP molecules.

Test results will be shown comparing the novel new fluorocarbons, [E]$CF_3$-CH=CHF; (1234ze(E)) and [E]$CF_3$ -CH=CHCl; (1233zd(E)) to existing fluorocarbons like $CF_3$-$CH_2F$; (HFC-134a) and $CF_3$-$CH_2$-$CHF_2$; (HFC-245fa), with tracking of the complete decomposition chain. Known atmospheric degradation products, 3-dimensional Global Warming Potentials are also reported. The results of a complete Life Cycle Analysis these two fluids compared to other fluorocarbons is also presented.

## B9.2

# Moderate Lewis acid metal fluoride with high specific surface area as catalyst for the fluorination of 2-chloropyridine by HF

**A. ASTRUC** [(a)]* , **S. CELERIER** [(a)], **S. BRUNET** [(a)]

[(a)] IC2MP, UMR 7285 - POITIERS (FRANCE)

* arnaud.astruc@univ-poitiers.fr

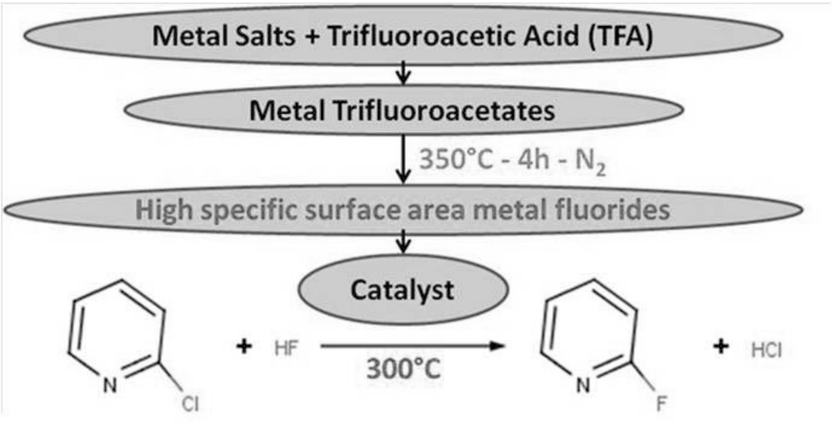

Fig. 1: Preparation of metal fluorides

Fluoropyridine compounds could be intermediates in the preparation of biologically active compounds such as herbicides, plant growth regulators, insecticides and fungicides [1]. These compounds are mainly synthesized by HALEX reaction in liquid phase with KF as the main fluoride source or by Balz-Schiemann reaction in the presence of HF. As an alternative, the aromatic nucleophilic substitution reactions in heterogeneous catalytic gas phase process from the corresponding chlorinated aromatics using HF as the fluorinated agent have many advantages. The Cl/F exchange requires only one step and the only by-product is HCl (potentially recyclable). Previous works [2,3] showed the possibility to obtain 2-fluoropyridine from the 2-chloropyridine by Cl/F exchange with HF gas and a heterogeneous metal fluoride catalyst. The selectivity of this reaction is of 100%. One of the key parameter to obtain high activity in these operating conditions (300°C under HF gas) is the specific surface area. Indeed, metal fluorides catalysts synthesized in-situ under HF flow from corresponding metal oxides have low specific surface areas [2]. One way is to prepare metal fluorides by “wet chemistry” leading to high specific surface area materials. In this work, metal fluorides ($BaF_2$, $MgF_2$, $CaF_2$, $ZnF_2$, $LaF_3$) were prepared by thermal decomposition of corresponding metal trifluoroacetates (fig. 1). The increase of the specific surface area allows to increase considerably the activity of these catalysts.

Moreover, the influence of the catalyst composition and the acidity properties, measured by CO adsorption followed by IR spectroscopy, on the fluorination of 2-chloropyridine were studied. Moderate strength of Lewis acidity promotes the reaction. Indeed, $BaF_2$ and $MgF_2$ were very active compared to the conventional fluorination catalyst, fluorinated chrome oxide, which has high strength of Lewis acidity.

From these results, a mechanism for the Cl/F exchange reaction was proposed.

This work was financially supported by ANR (Agence National de la Recherche).

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## B9.3

# Fluorination Catalysis for Halogen Exchange Chemistry in the Preparation of Low Global Warming Potential (L-GWP) Fluorocarbons

**S. SESHADRI** (a), **R.G. SYVRET** (a)*

(a) ARKEMA, INC., FLUOROCHEMICALS R&D - KING OF PRUSSIA (USA)

* robert.syvret@arkema.com

Low global warming potential (L-GWP) fluorocarbons are being developed as 4th generation environmentally acceptable candidates for service in refrigeration and foam expansion applications. Environmental awareness and adherence to mandates of the Montreal and Kyoto Protocols have led to the industrial progression from the original chlorofluorocarbons (CFCs) to 2nd generation hydrochlorofluorocarbons (HCFCs) to 3rd generation hydrofluorocarbons (HFCs) to the current 4th generation hydrofluoroolefins (HFOs). For example, 2,3,3,3-tetrafluoropropene (1234yf) is the leading L-GWP HFO candidate for mobile air conditioning applications. HFOs can be prepared in a number of ways, however, HF-based halogen exchange chemistry on chlorine containing olefins is the method used in almost all cases for industrial scale production.

Fluorination catalysts, both homogeneous and heterogeneous, are vital process components in the preparation of L-GWP fluorocarbons through halogen exchange chemistry. Homogeneous catalysts are employed in liquid phase halogen exchange reactions and are often based on chlorofluoro derivatives of Sb(V). Heterogeneous catalysts are used for gas phase halogen exchange reactions and are most often based on high oxidation state oxide fluorides of transition metals such as Cr(III) and Cr(IV).

There are many process factors that determine the performance, lifetime, and overall efficiency of a halogen exchange catalyst. Some of these factors include the method of preparation and activation, pressure, temperature and molar ratio of reactants, and the presence of co-fed reactants for stabilization. Each of these factors can greatly affect the economic viability of an industrial process.

In the present work we have focused on the critical process step of catalyst fluorination and activation. Some of our most recent results will be presented.

## IL-B10

# Triple Bond Systems of Sulfur

**R. MEWS (a)*, T. BORMANN (a), E. LORK (a), W.D. STOHRER (a), H. OBERHAMMER (b)**

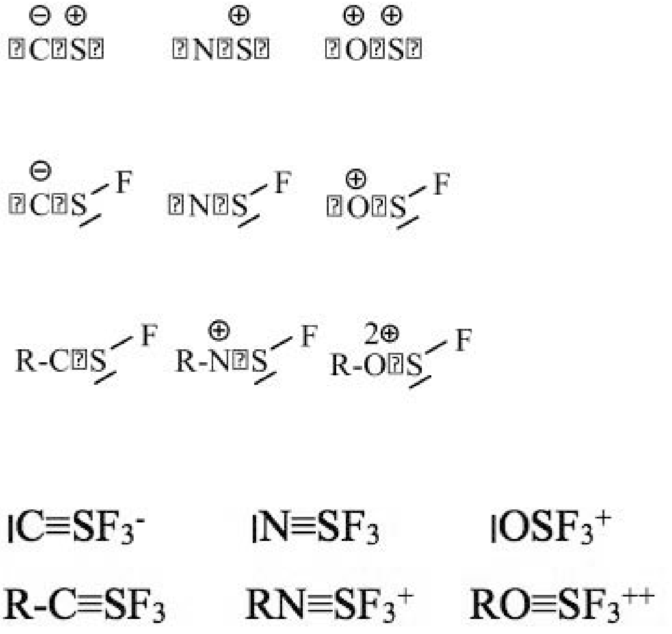
(a) DEPARTMENT OF CHEMISTRY, University of Bremen - BREMEN (GERMANY)
(b) Inst, of Phys.1 and Theor.1 Chem, University of Tübingen - TÜBINGEN (GERMANY)

* mewshome@uni-bremen.de

Fig. 1 shows the experimentally verified SN triple bond systems together with their (mostly unknown) isoelectronic CS and OS counterparts. After NSF [1] and $NSF_3$ [2] were reported in 1955, $[OSF_3]^+$ [3] and $RCSF_3$ (R= $F_3C$, $SF_5$[4]) followed in 1973 and 1984, respectively. From $NSF_{1,3}$ a large number of derivatives, of anionic and cationic triple bond species, of double and single bond species have been synthesized.

In addition to the species mentioned before, in carbon sulphur and oxygen sulphur chemistry only carbon monosulfide and HCSOH[5], an example of the RCSF-type, have been reported. Isoelectronic relationships with the NS-compounds, supported by theoretical calculations, might be guidelines for future experiments. NBO analyses are used for the classsification as triple bond species, resulting in a "triple bond map" for the CS, NS, and OS systems.

Of special interest is the influence of ligand exchange on structures and electronic properties. According to NBO analysis are $NS(CF_3)_2F$ and $NS(CF_3)_3$ triple bond species, $NSFPh_2$[6], however, not. The shortest sulfur element bonds are found in $[OSF_3]^+$ (135.8(4) pm) and $[H_3CNSF_3]^+$ (136.2(4) pm).



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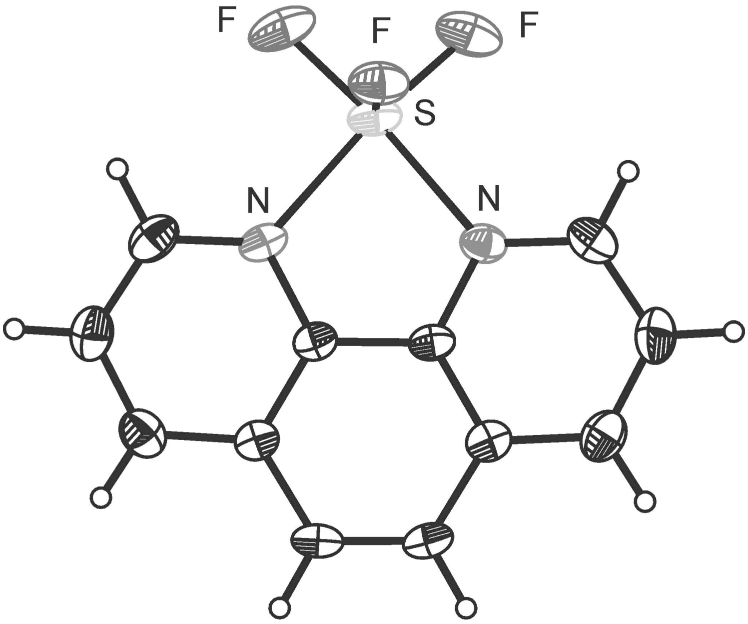
## B10.1

# Reactions of $SF_4$ and $SF_3^+$ with Lewis Bases

**P. CHAUDHARY** [(a)], **J. GOETTEL** [(a)], **H. MERCIER** [(b)], **P. HAZENDONK** [(a)], **M. GERKEN** [(c)]*

[(a)] University of Lethbridge - LETHBRIDGE (CANADA)
[(b)] McMaster University - HAMILTON (CANADA)
[(c)] UNIVERSITY OF LETHBRIDGE, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY - LETHBRIDGE (CANADA)

* michael.gerken@uleth.ca



Recently we could conclusively show the Lewis acid-base adduct formation between $SF_4$ and nitrogen-bases.[1] The series of Lewis acid-base adducts was extended to $SF_4$ adducts with oxygen bases, such as THF. The crystal structure of $SF_4$·THF contain dimers with weak bridging S···O···S interactions.

Lewis acid-base adducts between the $SF_3^+$ cation and the oxygen of C=O groups are thought to be intermediates in the fluorination reactions of C=O groups by $SF_4$. The reactions of $SF_3^+$ salts with a number of bases were studied. The reaction with the bases, pyridine and acetonitrile, yield the 1:2 cationic adducts, $[SF_3(NC_5H_5)_2]^+$ and $[SF_3(NCCH_3)_2]^+$. Salts of these cations were studied by $^{19}F$ NMR and Raman spectroscopy as well as X-ray crystallography. With 1,10-phenanthroline, the 1:1 adduct $[SF_3(phen)]^+$ (Figure 1) was obtained, as observed by X-ray crystallography. The stronger base, 4-dimethylaminopyridine is able to substitute fluorine atoms of the $SF_3^+$ cation, yielding a range of sulphur fluoride 4-dimethylaminopyridine adducts.

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[1] J. T. Goettel, P. Chaudhary, P. Hazendonk, H. P. A. Mercier, M. Gerken *Chem.Commun.*, **48.** (2012) **9120-9122**.

### B10.2

# Structures of Aromatic Radical Cations

**K. SEPPELT [(a)]* , M. KHANFAR [(b)], M. MOLSKI [(c)], H. SHORAFA [(c)]**

[(a)] Freie Universitaet, INSTITUT FUER CHEMIE UND BIOCHEMIE - BERLIN (GERMANY)
[(b)] University of Jordan - AMMAN (JORDAN)
[(c)] Freie Universitaet - BERLIN (GERMANY)

* seppelt@zedat.fu-berlin.de

While $C_6H_6^+$ has not clearly been identified in substance, $C_6F_6^+$ can be obtained in crystalline form 1), similarly $C_6Cl_6^+$, $C_6Br_6^+$, and $C_6I_6^+$. The influence of the *Jahn-Telle*r distortion is discussed in detail. The scope of this work is enlarged into partially halogenated and $CF_3$ substituted benzene radical cations.

Also larger aromatic radical cations derived from perfluoro biphenyl, perfluoro naphtaline, and perfluoro antracene can be isolated. These show considerable different structures then the neutral precursors.

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[1] *Angew. Chem. Int. Ed.* **2009**, *48*, 5845-5847

## B10.3

# Pentafluoroethyltinfluoride and Bis(pentafluoroethyl)stannylenes

**J. KLÖSENER** [(a)]* , **B. HOGE** [(a)]

[(a)] Bielefeld University, ANORGANIC CHEMISTRY II - BIELEFELD (GERMANY)

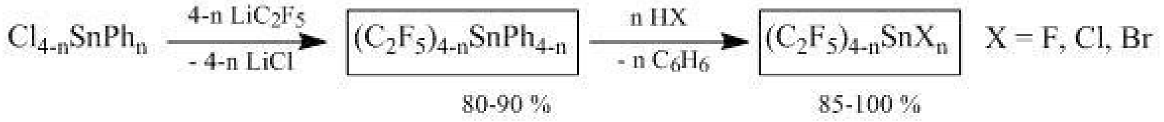
* johannes.kloesener@uni-bielefeld.de

The reaction of the chlorophenylstannanes $Cl_{4-n}SnPh_n$ (n = 1-3) with pentafluoroethyllithium lead to high yield syntheses of the pentafluoroethyl(phenyl)stannanes, $(C_2F_5)_{4-n}SnPh_n$. The subsequent reaction with hydrogenbromide or –chloride at elevated temperatures results in the formation of the corresponding tin halides, $(C_2F_5)_{4-n}SnX_n$ (X = Br, Cl) (Eq[1])

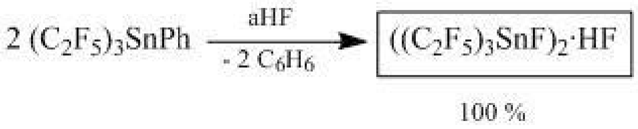
However, the reaction of tris(pentafluoroethyl)phenylstannane, $(C_2F_5)_3SnPh$, with anhydrous hydrogenfluoride proceeds already at ambient temperatures and a colorless solid is obtained. The product, an HF adduct of two $(C_2F_5)_3SnF$ molecules, can be interpreted in terms of a Brønsted acid. (Eq[2])

Treatment of the bromostannane $(C_2F_5)_2SnBr_2$ with tributyltinhydride at temperatures below -40 °C leads to the formation of bis(pentafluoroethyl)stannane, $(C_2F_5)_2SnH_2$. In non-coordinating solvents such as *n* -pentane and toluene it is stable at ambient temperature. The addition of a coordinating solvent such as ethers or acetonitrile initiates the reductive elimination of elemental hydrogen and formation of donor stabilized bis(pentafluoroethyl)stannylene. (Eq[3])

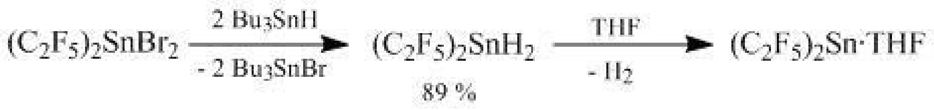
Depending on the reaction conditions, the stannylene exhibits a broad reactivity towards transition metal complexes.



$$Cl_{4-n}SnPh_n \xrightarrow[-\,4\text{-}n\ LiCl]{4\text{-}n\ LiC_2F_5} \underset{80\text{-}90\ \%}{\boxed{(C_2F_5)_{4-n}SnPh_{4-n}}} \xrightarrow[-\,n\ C_6H_6]{n\ HX} \underset{85\text{-}100\ \%}{\boxed{(C_2F_5)_{4-n}SnX_n}} \quad X = F, Cl, Br \qquad (1)$$



$$2\ (C_2F_5)_3SnPh \xrightarrow[-\,2\ C_6H_6]{aHF} \underset{100\ \%}{\boxed{((C_2F_5)_3SnF)_2\cdot HF}} \qquad (2)$$



$$(C_2F_5)_2SnBr_2 \xrightarrow[-\,2\ Bu_3SnBr]{<\ -40\ °C \atop 2\ Bu_3SnH} \underset{89\ \%}{(C_2F_5)_2SnH_2} \xrightarrow[-\,H_2]{THF} (C_2F_5)_2Sn\cdot THF \qquad (3)$$

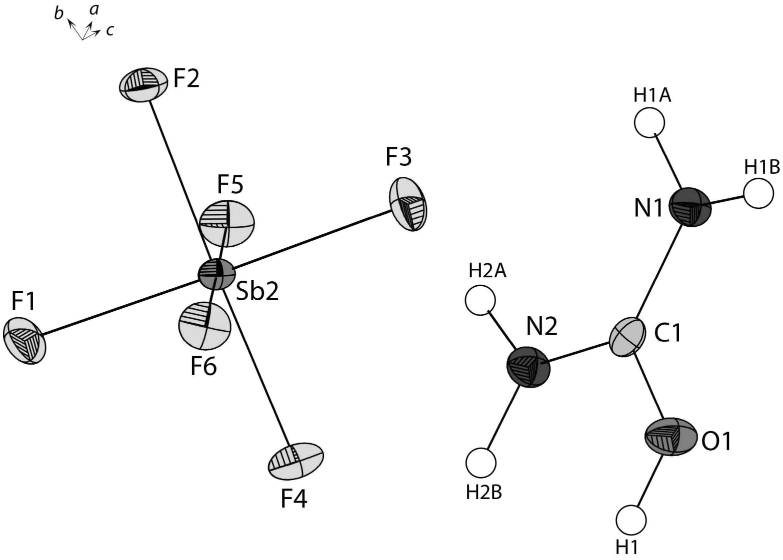
## B10.4

# PROTONATION OF UREA AND THIOUREA IN SUPERACIDS

**A. KORNATH** [(a)]*, **J. AXHAUSEN** [(b)], **K. LUX** [(a)]

[(a)] LUDWIG-MAXIMILIAN UNIVERSITY, DEPT. OF CHEMISTRY - MUNICH (GERMANY)
[(b)] LUDWIG-MAXIMILIAN UNIVERSITY - MUNICH (GERMANY)

* andreas.kornath@cup.uni-muenchen.de



The behavior of urea and thiourea in strongly acidic media is of notable interest because these molecules have two competing basic sites, on the one hand the nitrogen atom and on the other hand the oxygen or sulfur atom. Studies on the enzyme urease show a coordination of urea at the oxygen atom in a binding pocket followed by protonation of one nitrogen atom and elimination of ammonia. NMR and single crystal X-ray studies prove a protonation at the chalcogen (oxygen/sulfur) under formation of $[H2N(COH)NH2]^+$ and $[H2N(CSH)NH2]^+$ respectively. NMR spectroscopic investigations of thiourea in fluorosulfuric acid indicated S,N-diprotonated thiourea, whereas Olah Et Al. found indications for a dication only when antimony(V)-fluoride is added to the solution. In current studies the existence and possible structures of di- and triprotonated urea and thiourea are discussed primary on quantum chemical calculations. One possible structure of diprotonated thiourea is N,N-diprotonated thiourea, that is isostructural to acetone and was found to be 11.2 kcal/mol less stable than S,N-diprotonated structures, but experimental studies indicate S,N-diprototanted thiourea.

We have studied urea and thiourea in the superacidic systems HF/AsF5 and HF/SbF5. The vibrational spectra and single crystal x-ray structures of the resulting protonated species are discussed together with quantum-chemical calculations.

# STREAM FMEC

## THURSDAY, JULY 25

## IL-FMEC7

# F-based materials for Li-ion batteries

**J.M. TARASCON** [(a)]*

[(a)] LRCS, UMR 7314, Université de Picardie Jules Verne - AMIENS (FRANCE)

* jean-marie.tarascon@u-picardie.fr

Fluorine is a common component for Li-ion batteries. It can be found either in binders (PVDF-HFP), salts ($LiPF_6$), coatings or electrodes. F is among the most attractive elements to increase the redox potential of electrode materials, therefore its increasing use to design high voltage electrode materials. Combining both highly electronegative polyanions ($SO_4^{2-}$) and F- we have prepared a new class of polyanionic compounds $AMSO_4F$ (A= Li, Na, K and M=Mn, Fe, Co, Ni, Zn) which present both a rich crystal chemistry together with attractive electrical properties. Among them, triplite $LiFeSO_4F$ shows the highest potential (3.9 V vs. $Li^+/Li°$) ever reported for $Fe^{3+}/Fe^{2+}$ in inorganic compounds while LiZnSO4F displays good ionic conductivity. Such properties and their relation to practical applications will be discussed.

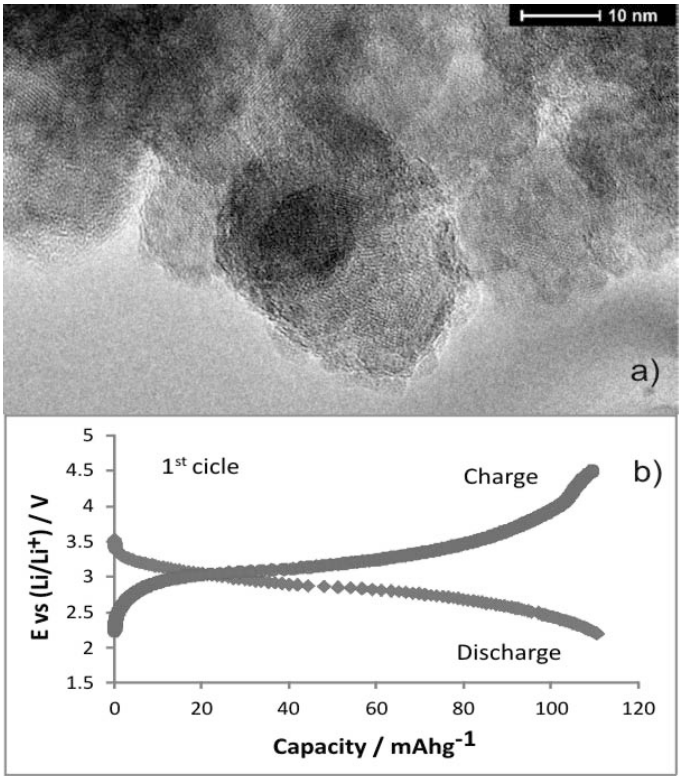
## FMEC-7.1

# Electrochemical properties of thermally activated $Li_3FeF_6$ as a cathode material in lithium secondary cells.

**A. BASA** [a] *, **K. PIETROWSKA** [a], **M. PERKOWSKI** [a], **S. WOJTULEWSKI** [a], **A.Z. WILCZEWSKA** [a], **E. GONZALO** [b], **A. KUHN** [c], **F. GARCIA-ALVARADO** [c]

[a] Institute of Chemistry, University of Bialystok - BIALYSTOK (POLAND)
[b] CIC ENERGIGUNE, Parque Tecnológico de Alava - MIÑANO (ALAVA) (SPAIN)
[c] Universidad San Pablo-CEU, Departamento de Quimica - BOADILLA DEL MONTE, MADRID (SPAIN)

* abasa@uwb.edu.pl



The complexes of transition metal fluorides seem to be very interesting as new materials applied to production of cathodes in reachable lithium batteries. The considerable electro negativity of fluorine increases the polarizability of M-F bonds, what cause the rise of the metal reduction potential. In consequence it increases the energy density stored in battery. Monoclinic (α-polymorph) and orthorhombic (β-polymorph) crystal structure of $Li_3M^{III}F_6$, similar to three dimension cryolite structure, allow to occur of the reversible process of lithium intercalation/deintercalation [1,2,3]. Unfortunately complexes of transition metal fluorides have the poor electronic conductivity and needs the activation by ball milling with addition of carbon [2,4].

The aim of research was the thermal activation of α-$Li_3FeF_6$. The complex was synthetized by precipitation in room temperature from the water solution by addition of 2-propanol [4]. The synthesis route leads to obtain 20 nm particles, which are agglomerated in more than 200 nm hollow spheres. The samples were heating in ambient atmosphere in wide range of temperatures and time periods. Heat treatment develops surface of material by opening structure of hollow spheres and causes to creation of more isolated 20 nm particles. As prepared $Li_3FeF_6$, was mixed manually with carbon.

80% of the theoretical capacity (140 $mAhg^{-1}$) has been achieved in experimental cells for thermally activated α-$Li_3FeF_6$. The purity of sample was tested with use of the X-Ray diffraction and Raman Spectroscopy technics. The morphology was study by TEM and SEM microscopy and porosimetry measurements. Chemical and physical modifications of the α-$Li_3FeF_6$ hollow sphere surface, which take place during heating and lead to the electrochemical activation of α-$Li_3FeF_6$, still need the further investigations.

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[4] A. Basa, E. Gonzalo, A. Kuhn, F. García-Alvarado, *J .Power Sources* **197** (2012) 260.

**FMEC7.2**

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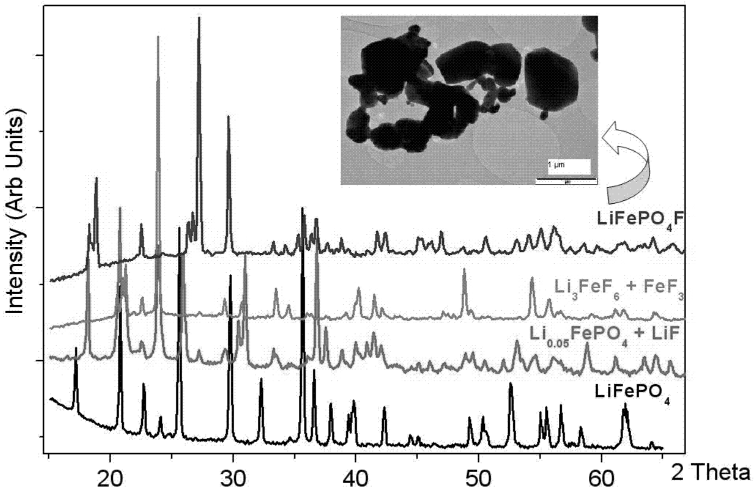
# Synthesis of $LiFePO_4F$ by solid-gaz reaction: revisiting the ceramic method

**P. BONNET [a]*, R. KEMOGNE-DEBAH [a], N. LOUVAIN [a], L. FREZET [a], C. FONQUERNIE [a], M. EL-GHOZZI [a], K. GUERIN [a], B. DEVOUARD [b], P. WILLMANN [c]**

[a] INSTITUT DE CHIMIE DE CLERMONT FERRAND - AUBIERE CEDEX (FRANCE)
[b] CEREGE - MARSEILLE (FRANCE)
[c] CNES - TOULOUSE (FRANCE)

* pierre.m.bonnet@univ-bpclermont.fr

Inorganic fluorides like iron fluoride $FeF_3$, lithiated iron fluoride $Li_3FeF_6$, $A_2$ MPO4F and $AMPO_4F$ fluorophosphates (A = Na, Li; M = Fe, Mn, Co, Ni), $Li(Fe_{1-x} M_x)SO_4F$ fluorosilicate, etc. appear good solutions for Li-ion technology. Indeed, fluoride-based electrodes display greater potential due to the larger ionicity of M–F bonds as compared to M–O bonds. Solid-state synthesis, aqueous hydrothermal/solvothermal or ionothermal synthesis have been reported for the elaboration of these materials.



*XRD patterns of pristine $LiFePO_4$ and materials obtained by fluorination of $LiFePO_4$ . Insert: TEM picture of $LiFePO_4F$.*

Here, the fluorination of $LiFePO_4$ by molecular fluorine ($F_2$) is performed between room temperature and 500°C and we report for the first time the synthesis of $LiFePO_4F$ by a method based on gas-solid reaction. The insertion of fluorine in the phosphate matrix has been studied as a function of experimental conditions. Structural characterizations (XRD, Raman and TEM) indicate that fluorine atoms trend to extract Li atoms from the matrix leading to a delithiated iron phosphate compound. Above 250°C, the fluorination of the iron phosphate matrix occurs and the $LiFePO_4F$ phase is observed. If the fluorination is performed above 500°C, the phosphate matrix is totally destroyed and electrodes materials composed of a mixture of $FeF_3$ and $Li_3FeF_6$ are obtained. In this study, we demonstrate that several electrodes materials can be synthesized by direct fluorination of $LiFePO_4$, according to the experimental conditions. Finally, electrochemical properties of the fluorinated phases have been also investigated.

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## FMEC-7.3

# Remarkable transformation of fluorine from a small exotic element into highly valued and mature participant in energy conversion and storage systems

**D.T. MESHRI [(a)]*, N.C. MATHUR [(a)], R. ADAMS [(a)], S. MESHRI [(a)], R. JAIN [(a)], D. PINNAPAREDDY [(a)]**

[(a)] Advance Research Chemicals, Inc - CATOOSA (USA)

* dr.meshri@fluoridearc.com

Henri Moissan isolated fluorine in 1886 for the first time and the modern field of fluorine chemistry was born. Dramatic changes had happened since then and now there is not a single area in our daily life where fluorine or its products are not used. Increased usage of fluorine is due to unique properties of fluorinated materials which are due to very high electro-negativity, high ionic potential and low polarizability of the fluorine atom.

With all new developments and growth and human quest for improving quality of life, energy needs are also rising up and up. Efforts are being made to continuously explore new fossil resources, develop alternative forms of energy and improve energy efficiency. The development of portable electronics in last two decades has led to more research on electrode materials, electrolytes, additives, separators, etc. with the aim to improve the performance of energy storage devices like batteries, capacitors and fuel cells.

Fluorine and fluorinated materials play important role in energy systems from UF6 processing in nuclear energy to fuel cells and batteries. In this presentation, role and impact of fluorine and fluorinated materials in energy system shall be highlighed.

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## IL-FMEC8

# Batteries based on metal halides

**M. FICHTNER** [(a)(b)*], **M.A. REDDY** [(b)], **B. BREITUNG** [(b)], **V.S.K. CHAKRAVADHANULA** [(a)(b)], **B.K. DAS** [(a)],
**C. RONGEAT** [(b)], **D. WANG** [(b)], **X. ZHAO** [(b)]

[(a)] HELMHOLTZ INSTITUTE Ulm, Ulm University - ULM (GERMANY)
[(b)] KARLSRUHE INSTITUTE OF TECHNOLOGY, Institute of Nanotechnology - KARLSRUHE (GERMANY)

* m.fichtner@kit.edu

The application of conversion materials in electrochemical storage devices is one of the very few options to build batteries with considerably increased energy densities. Many conversion based systems seem to be interesting due to their high theoretical energy densities [1]; however, there are practical issues such as reversibility and kinetics leading to fading capacities during cycling and/or to comparably low power density and voltage hysteresis. These barriers have been addressed by various groups [2] and recent progress will be shown which was obtained with novel and facile synthesis approaches [3].

In the search for Li-free systems with higher storage capacities the application of different charge transfer systems based on singly charged negative ions may be beneficial. For example, the reaction of highly electronegative fluorine with metal leads to the formation of metal fluorides which are accompanied by large change in free energy and thus high electromotoric force [4]. Recently, we showed that by choosing appropriate metal/metal fluoride combinations, electrochemical cells can be built with theoretical gravimetric and volumetric energy densities which exceed the theoretical potential of current Li ion batteries by an order of magnitude. The key success of fluoride ion battery is largely dependent on the fluoride ion transport media. It was known that the tysonite $MF_3$ (M= La and Ce) and fluorite $MF_2$ (M= Ca, Sr and Ba) type compounds are super fluoride ion conductors at high temperatures. However, when they are doped with aliovalent fluorides they conduct at moderate temperatures. Electrochemical cells have been built with metal fluorides as cathode, tysonite or fluorite-based electrolyte and La or Ce as the anode. The analysis of the electrode confirms the reversible fluoride transfer between the two electrodes [5].

The concept was developed further to also build secondary “Chloride Ion Batteries” which are based on $Cl^-$ as charge transfer ion. They work also with liquid electrolytes, do not necessarily contain lithium and have theoretical energy densities which are considerably beyond that of the current Li ion battery [6].

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## FMEC8.1

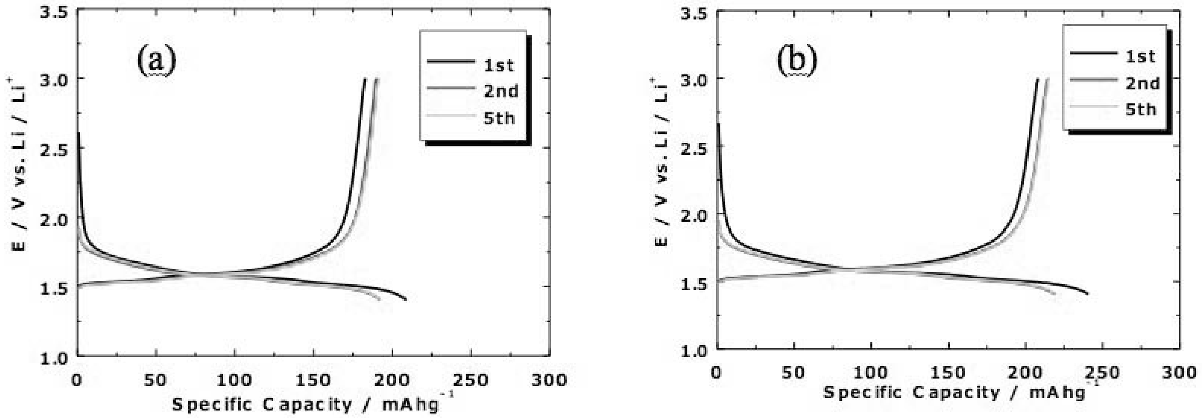
# Effect of Surface Fluorination on the Charge/discharge Properties of High Potential Negative Electrode $TiO_2$(B) for LIBs

**A. TASAKA** [(a)]*, **M. SAITO** [(a)], **Y. NAKANO** [(a)], **M. TAKAGI** [(a)], **T. MAEKAWA** [(a)], **H. TAKEBAYASHI** [(b)], **Y. SHODAI** [(b)], **M. INABA** [(g)]

[(a)] Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshiba University - KYOTO (JAPAN)
[(b)] Kondo Teruhisa Memorial Advanced Carbon Technology Center, Toyo Tano Co., Ltd. - OSAKA (JAPAN)

* aki_tasaka_load@yahoo.co.jp

Surface fluorination of $TiO_2$(B) powder was conducted by pure $F_2$ gas at room temperature for 1 h and the effect on the charge/discharge properties was examined as a negative electrode of Li-ion batteries (LIBs). X-ray diffraction (XRD) pattern was not changed before and after the surface fluorination though the peak intensities became weaker than that of the pristine sample, indicating the etching of the surface of SF-$TiO_2$ (B) powder. This was supported by scanning electron microscopy (SEM) observation. However, X-ray photoelectron spectroscopy (XPS) analysis clearly revealed that F atoms exist on the surface of $TiO_2$(B) particles and probably were covalently bonded with Ti atoms near the surface. From the charge/discharge tests at a C/6 rate, as shown in Fig. 1, the SF-$TiO_2$(B) exhibited a higher 1st discharge (203 mAh $g^{-1}$) than the pristine sample (181 mAh $g^{-1}$) with a good cycleability. Impedance analysis revealed that both resistances of solid electrolyte interphase (SEI) film and charge transfer at the SEI /active material interface were reduced by surface fluorination, implying the improvement of SEI film and permeability of the electrolyte solution to the interphase. The rate capability was improved by the surface fluorination up to 1C rate, at which the SF-$TiO_2$(B) exhibited a high discharge capacity of around 150 mAh $g^{-1}$.



*Charge/discharge curves of (a) pristine and (b) SF-$TiO_2$(B) betwewn 1.4 and 3.0 V at C/6 rate in 1 M $LiPF_6$/EC+DMC (1:2)*

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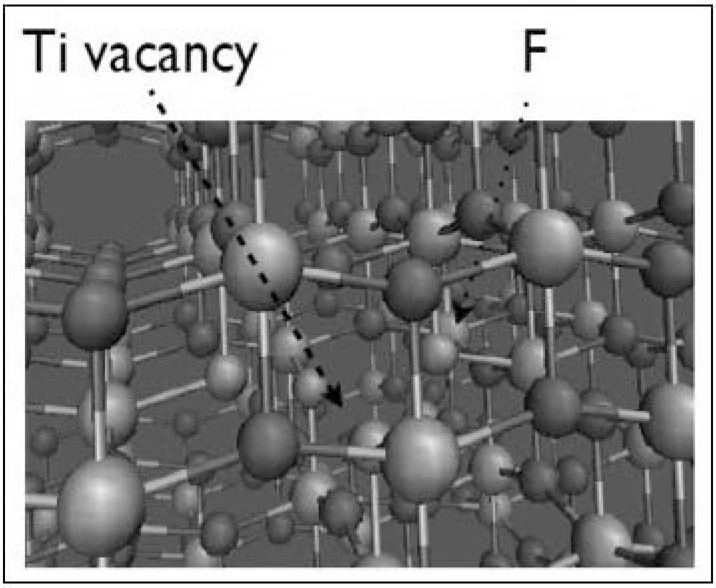
## FMEC8.2

# Titanium oxyfluoride having the anatase type structure: Short-long range orders and electrochemical properties

**D. DAMBOURNET** [(a)]*, **W. LI** [(a)], **D. CORRADINI** [(a)], **M. SALANNE** [(a)], **A.L. ROLLET** [(a)], **C.M. JULIEN** [(a)], **H. GROULT** [(a)], **K. ZHAGIB** [(b)], **C. LEGEIN** [(c)], **M. BODY** [(c)], **K. CHAPMAN** [(d)], **P. CHUPAS** [(d)]

[(a)] LABORATOIRE PECSA, UPMC - CNRS UMR 7195 - PARIS (FRANCE)
[(b)] Institut de Recherche d'Hydro-Quebec - VARENNES (CANADA)
[(c)] Université du Maine - LE MANS (FRANCE)
[(d)] X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory - ARGONNE (USA)

* damien.dambournet@upmc.fr



*Snapshot of the Anatase showing a cationic vacancy*

Among the 9th most abundant elements on earth, titanium, a 3d transition metal, is currently one of the most studied element in physical chemical sciences.Owing to its electronic properties, titanium dioxide is currently investigated for a large range of applications ranging from photocatalysis to energy storage. Downsizing the solid particles has been one of the first approaches to tailoring the physical-chemical properties of $TiO_2$.

Herein, we report on the modification of the chemical composition of titanium oxide with the partial substitution of $O^{2-}$ by $F^-$, creating cationic vacancies within the lattice (Scheme 1). Experimental and computational data have been implemented in order to understand the local and long range structural order occurring in the defective solid.

The impact of the structural features on the electrochemical properties *vs.* Li insertion/extraction will be presented. The role of the cationic vacancies on the rate capability will be also emphasized. In terms of cycleability, it will be shown that these materials give rise to impressive performances when they are used in Li-ion battery. Thus, the charge/discharge rate can be about 10 times higher than for stoichiometric $TiO_2$ anatase.

## IL-FMEC9

# New Fluorine-containing Cathode Materials for Li-ion batteries

**E. ANTIPOV** [(a)]*, **N. KHASANOVA** [(a)], **O. DROZHZHIN** [(a)]

[(a)] MOSCOW STATE UNIVERSITY, DEPARTMENT OF CHEMISTRY - MOSCOW (RUSSIA)

* evgeny.antipov@gmail.com

Li-ion batteries originally developed for portable devices can now be found in applications as diverse as power tools, electric vehicles and stationary energy storage. To satisfy the need of current and new applications, Li-ion batteries require further improvement in terms of performance properties (energy and power density, safety and cost).

First generation of cathode materials for Li-ion batteries representing the ternary mixed oxides with spinel or rock-salt derivatives structures has been already widely commercialized. However, these materials have severe limitations in further improvements of their properties related to their structural features. Transition metal compounds containing different polyanion units $(XO_n)^{m-}$ (X=B, P and Si) are now considered as promising cathode materials for next generation of Li-ion batteries.

Further advances in the polyanion-containing cathode materials are related to combining $(XO_n)^{m-}$ and $F^-$ in the anion sublattice, which is expected to enhance specific energy of these materials. Indeed, various fluorine-containing sulphates and phosphates have been recently discovered, and some of them exhibit attractive electrochemical performance. Fluorine-containing phosphates of the general formula $Li_2MPO_4F$ have received particular interest due to their potential to operate on more than one alkali atom per formula unit, which would result in higher specific capacity and energy density. These materials crystallize in different structure types (2 or 3-dimensional ones) with distinct arrangement of $MO_4F_2$ octahedra and $PO_4$ tetrahedra thus resulting in variation of operating voltage and diffusion pathways for Li-ions. Three different modifications of $Li_2FePO_4F$ can be obtained by application of different way of synthesis [1-4]. The overview of our recent research activity on fluorine-containing cathode materials ($Li_2MPO_4F$) with M = Co or Fe for Li-ion batteries will be presented.

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## IL-FMEC10

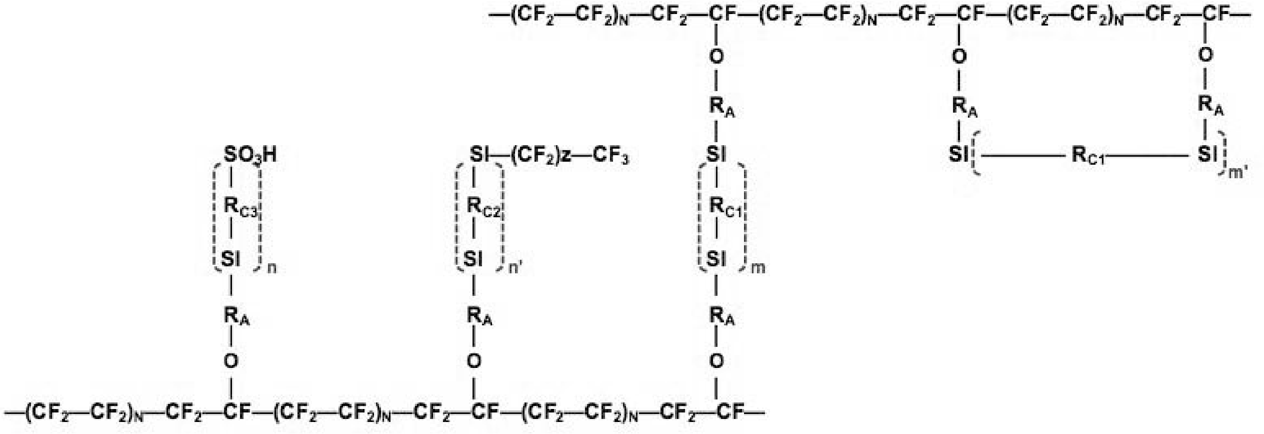
# Novel Low EW, Water Insoluble Perfluorosulfonimide (PFSI) Ionomers

**J.S. THRASHER** [(a)]* , **A.V. MATSNEV** [(a)], **T.S. SAYLER** [(b)], **R.E. FERNANDEZ** [(a)], **A. WATERFELD** [(b)]

[(a)] Department of Chemistry, Clemson University, Advanced Materials Research Laboratory - ANDERSON, SC (USA)
[(b)] Department of Chemistry, The University of Alabama - TUSCALOOSA, AL (USA)

* thrash5@clemson.edu

Perfluorosulfonimide (PFSI) ionomers were first prepared by DesMarteau and co-workers [1], and these electrolyte materials were generally found to be superior when compared to perfluorosulfonic acid ionomers (PFSA) such as Nafion® [2]. However, if one attempts to prepare lower equivalent weight (EW) materials with increased conductivity to meet today's demand for PEM fuel cells to operate at 120 °C and low relative humidity, then these ionomers generally suffer from greatly reduced mechanical strength, and they eventually become water soluble. An approach that can be used to combat the loss of mechanical strength and to prevent water solubility is to add some crosslinks between the polymer chains, as has been done by Uematsu and co-workers at Asahi Kasei Corporation [3]. We have used an alternate crosslinking approach to prepare low EW, water insoluble PFSI ionomers that display significantly greater conductivity at low relative humidity (10-20%) than Nafion® membranes of comparable thickness [4]. A three- or four-step process is used to prepare the novel PFSI ionomers shown in Figure 1: (1) prepare a low EW PFSA resin from either TFE and PSEPVE or TFE and Dow vinyl ether, (2) convert the PFSA resin to its corresponding sulfonamide resin by reaction with ammonia, (3) treat the sulfonamide resin with a sulfonimide (SI) oligomer with sulfonyl fluoride end groups, and (4) retreat the resulting resin with either the same SI oligomer or another difunctional sulfonyl fluoride to convert all sulfonamide groups to sulfonimide linkages. Reaction work-up generally includes hydrolysis, acidification, and purification.



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## FMEC10.1

# Nano-structured aromatic ionomers partially fluorinated for PEMFC

**L. ASSUMMA** (a)*, **C. IOJOIU** (a), **R. MERCIER** (b), **S. LYONNARD** (c)
(a) UNIVERSITÉ DE GRENOBLE, LEPMI - SAINT MARTIN D'HÈRES (FRANCE)
(b) IMP UMR 5223 - VILLEURBANNE (FRANCE)
(c) CEA, INAC, SPrAM - GRENOBLE (FRANCE)
* cristina.iojoiu@lepmi.grenoble-inp.fr

The core of the proton exchange membrane fuel cell (PEMFC) is a membrane (PEM) that allows the transport of protons, evolved at the anode, to the cathode where oxygen is reduced to produce water. Different membranes based ionomers were investigated as PEM, the most famous from them being the perfluorsulfonated polymer, Nafio®, which consists of an extremely high hydrophobic perfluorinated backbone along with an extremely high hydrophilic sulfonic acid functional groups. Despite their advantages, existing drawbacks make questionable their use in PEMFC hence, great efforts have been devoted to searching high-performance aromatic ionomers as alternative materials to Nafion[1]. Many works investigated the sulfonated aromatic polymers were the sulfonic acid was grafted on the main chain. However they show sufficiently high conductivities only at high IECs. But high IECs cause extensive water uptake and consequently a dramatic loss of mechanical strengths that renders them unsuitable for practical PEM applications. Kreuer et al.[2] reported that typical sulfonated aromatic polymers are unable to form defined hydrophilic domains, as the rigid aromatic backbone prevents the formation of continuous conducting channels. These issues can be sorted out by fine-tuning several parameters such as ionic function acidity, main-chain and/or side chain structures. One promising approaches concerns the block copolymers whereby acidic ionic groups are concentrated in one of the blocs along with the polymer chain [3].

This publication deals with the synthesis and characterisation of new block copolymers hydophilic-hydrophobic based on partially perfluorinated aromatic ionomers. The hydrophilic blocks are functionalized with perfluorosulfonic acid while the hydrophobic blocs are partially perfluorinated. The polymer main chain was synthetised by polycondensation, the perfluorsulfonic acid functions were grafted by Ullman reaction [4]. The superacidity of ionic function, the flexibility of the spacer between the acidic function and the main chain, the structure of the main chain allow to obtain very well nanostructurated membrane. The relationship between the membrane morphology, evidenced by SANS, AFM, TEM, and the thermo-mechanical, electrochemical properties and fuel cell performances will be deeply discussed.

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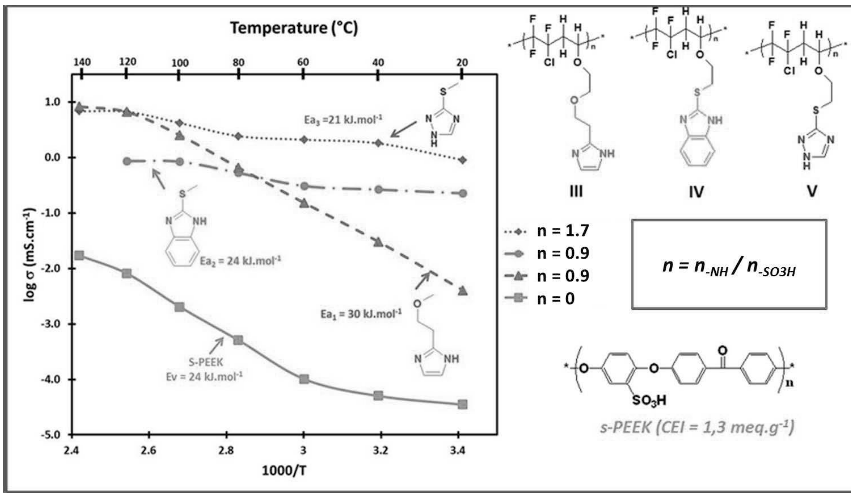
## FMEC10.2

# Novel blend membranes for PEMFC based on s-PEEK and fluorinated copolymers bearing azole (imidazole, benzimidazole or triazole) compounds: A study on N-heterocycle nature.

**B. CAMPAGNE** [(a)]* , **D. GHISLAIN** [(a)], **B. AMEDURI** [(b)], **D.J. JONES** [(a)], **R. JACQUES** [(a)], **I. ROCHE** [(c)]

[(a)] ICGM-IAM, IAM AND AIME - MONTPELLIER (FRANCE)
[(b)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)
[(c)] PSA-Peugeot Citroën - VéLIZY VILLACOUBLAY (FRANCE)

* benjamin.campagne@enscm.fr



In order to overcome different issues of perfluorosulfonic acid (PFSA) based membranes such as water management and catalyst (Pt) CO poisoning, new Proton Exchange Membranes Fuel Cell (PEMFC) membranes working at medium temperatures (120 – 180 °C) and under quasi-anhydrous conditions (RH < 30 %) were synthesized and characterized. These new blend membranes were composed of a partially fluorinated copolymer bearing imidazole (1), benzimidazole or 1,2,4-triazole as pendant groups and sulfonated PEEK (s-PEEK). Synthesis of the different fluorinated copolymers bearing azole functions (imidazole, benzimidazole or 1,2,4-triazole) as pendant groups were carried out and the thermal and chemical properties of the resulting products were assessed. The fluorinated copolymers containing azole functions were then blended with s-PEEK to obtain membranes by film casting. S-PEEK allowed ensuring enough mechanical stability to the membrane but also allowed acid doping due to the presence of sulfonic acid functions of s-PEEK (IEC = 1.3 meq.g-1). Proton transport of these membranes was achieved by « proton hoping / azole re-orientation » (2) mechanism due to the presence of azole groups that acted as immobilized solvent. Proton conductivity values of membranes were assessed and reached 6 - 7 mS.cm-1 at 145 °C under quasi-anhydrous conditions (RH < 30 %) (3).The influence of the nature of the N-heterocyclic compound was studied.

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## FMEC10.3

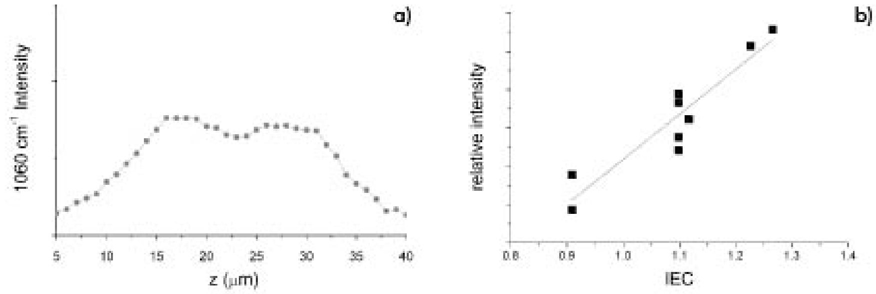
# Characterization by micro-Raman spectroscopy of tri-layer PFSA membrane for PEM fuel cells

**C. BAS** [(a)]* , **J. GUIRONNET** [(a)], **A. EL KADDOURI** [(a)], **E. MOUKHEIBER** [(a)], **G. DE MOOR** [(a)], **L. FLANDIN** [(a)]

[(a)] LEPMI - UNIVERSITE DE SAVOIE, UMR 5279 - LE BOURGET-DU-LAC (FRANCE)

* corine.bas@univ-savoie.fr

The Raman spectra of commercial Perfluorosulfonic acid (PFSA) ionomer membranes were recorded using a Raman microscope in confocal or plan mode (Fig.1). In the recent publications, the microRaman was successfully employed for the determination of water content [1-4]. The present study concerns a reinforced PFSA (XL100®). The absorption bands were accordingly separated in four categories with similar behaviors. The relative intensities of several absorption bands was carefully measured varying the length of the side chain, and the ion exchange capacity (IEC) (Fig.2). The assignments reported in the literature [5-7] for the fundamental vibrations observed for this material will be discussed. On the application standpoint, a strong relationship between the relative intensity at 800 cm-1 and the chemical structure allows an accurate determination of IEC in tri-layer PFSA (XL100®).



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## IL-FMEC11

# Akema's advances in fluorochemical technologies for lithium ion battery

**P. BONNET** [(a)]*, **G. SCHMIDT** [(a)], **J. CHAUVEAU** [(b)]

[(a)] ARKEMA, CENTRE DE RECHERCHES RHôNE ALPES - PIERRE BENITE CEDEX (FRANCE)
[(b)] ARKEMA CERDATO - SERQUIGNY (FRANCE)

* philippe.bonnet@arkema.com

The actual development of Li-ion batteries for applications such as mobile technologies, electrical vehicles and stationary energies require improvements of performance and safety. From a performance standpoint, the increase of lifetime, energy and power density are key factors.
This presentation is dealing with the tuning of two elements of the battery to increase performances:

- the binder, an essential piece for the electrode integrity
- the electrolyte, one of the key component of the battery

Arkema has developed new grades of fluoropolymer based binders that improve the battery lifetime and reduce loading for electrode manufacturing by solving the battery failures that are due to a lack of adhesion or cohesion.
For new nano scale active materials (HE or HV lithium) or for specific electrode design, Arkema has also developed new technologies based on functionalized homopolymer and copolymer resins. The functionality boosts the adhesion and the cohesion at all the electrode interfaces and helps preventing the loss of electrical contacts in stringent conditions.

Despite the addition of additives into the electrolyte, the $LiPF_6$ based electrolyte shows limitations in terms of chemical and electrochemical stability like manganese dissolution, water and thermal instability. This presentation will demonstrate the advantages of new electrolytes based on two new salts PEA and LEA, i.e

- the impact of the high chemical stability (in presence of water ) of LEA on safety and lifetime of the battery.
- how the electrochemical stability (5.5 V) and the high ionic conductivity of PEA allows the increase of the power and energy density by using new cathode materials.

## FMEC11.1

# Safety improvement of lithium ion battery by fluorine compounds having low reactivity with Li and high oxidation stability

**T. NAKAJIMA [a]*, D. NISHIKAWA [a], Y. OHZAWA [a], M. KOH [b], A. YAMAUCHI [b], M. KAGAWA [b], H. AOYAMA [b]**

[a] DEPARTMENT OF APPLIED CHEMISTRY, AICHI INSTITUTE OF TECHNOLOGY - TOYOTA (JAPAN)
[b] DAIKIN INDUSTRIES, LTD. - SETTSU (JAPAN)

* nakajima-san@aitech.ac.jp

Reactivity with Li or $LiC_6$ and electrochemical oxidation stability of fluorine compound-mixed electrolyte solutions have been investigated by DSC and oxidation current measurements. Charge/discharge behavior of natural graphite electrode (NG15 μm) has been also examined using the same electrolyte solutions. Fluoro-sulfonate did not react with metallic Li below 300˚C, and fluoro-carbonates had much lower reactivity with metallic Li than EC/DMC. The 1 $molL^{-1}$ $LiPF_6$-EC/DMC/fluorine compound (1:1:1 vol.) and 0.67 $molL^{-1}$ $LiPF_6$-EC/DEC/fluorine compound (1:1:1 vol.) showed the lower reactivity with $LiC_6$ between 100 and 150˚C, and the smaller exothermic peaks by decomposition of the solutions and surface films than 1 $molL^{-1}$ $LiPF_6$-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.) without fluorine compound, respectively. Low reactivity of fluorine compounds with Li and $LiC_6$ may be due to the electron-withdrawing ability of fluorine atom, which reduces electron density of oxygen atoms in fluorine compounds. Oxidation currents measured using glassy carbon were smaller in 1 $molL^{-1}$ $LiPF_6$-EC/DMC/fluorine compound (1:1:1 vol.) and 0.67 $molL^{-1}$ $LiPF_6$-EC/DEC/fluorine compound (1:1:1 vol.) than in 1 $molL^{-1}$ $LiPF_6$-EC/DMC (1:1 vol.) and 1 $molL^{-1}$ $LiPF_6$-EC/DEC (1:1 vol.), respectively. First coulombic efficiencies and capacities obtained in 1 $molL^{-1}$ $LiPF_6$-EC/DMC/fluorine compound (1:1:1 vol.) and 0.67 $molL^{-1}$ $LiPF_6$-EC/DEC/fluorine compound (1:1:1 vol.) were similar to those in original 1 $molL^{-1}$ $LiPF_6$-EC/DMC (1:1 vol.) and -EC/DEC (1:1 vol.). Mixing of fluorine compound is quite effective for improving the charge/discharge behavior of propylene carbonate (PC)-containing electrolyte solution. First coulombic efficiencies highly increased in 1 $molL^{-1}$ $LiPF_6$ -EC/EMC/PC/fluorine compound (1:1:1:0.33 or 1:1:1:1.5 vol.), compared with that obtained in 1 $molL^{-1}$ $LiPF_6$ -EC/EMC/PC (1:1:1 vol.). Considering the results obtained by DSC, oxidation current measurement and charge/discharge cycling, fluoro-sulfonate and fluoro-carbonates are suitable as new solvents having low reactivity with Li and high oxidation stability for lithium ion battery.

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[1] Y. Matsuda, T. Nakajima, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, H. Aoyama, *J. Fluorine Chem.*, **132** (2011) 1174-1181.
[2] N. Ohmi, T. Nakajima, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, H. Aoyama, *J. Power Sources*, **221** (2013) 6-13.

## FMEC11.2

# Synthetic approaches for new components of lithium battery electrolytes

**T. BOETTCHER** [(a)], **N. KALINOVICH** [(a)], **O. KAZAKOVA** [(a)], **K. VLASOV** [(a)], **M. PONOMARENKO** [(a)], **R. SCHMITZ** [(b)], **M. WINTER** [(b)], **G. ROESCHENTHALER** [(a)]*

[(a)] JACOBS UNIVERSITY BREMEN GGMBH, SCHOOL OF ENGINEERING AND SCIENCE - BREMEN (GERMANY)
[(b)] School of Engineering and Science, Jacobs University Bremen - BREMEN (GERMANY)

* g.roeschenthaler@jacobs-university.de

Starting from hexafluoropropene oxide a new co-solvent for PC-based electrolytes for lithium-ion batteries could be synthesized.[1, 2] Fluorosulfonyldifluoroacetic acid fluoride is a very useful precursor for a lithium sulfonate, which could be applied as a new conducting salt.[3] From the same precursor a cyclic sulfonamide is available as a versatile SEI-forming additive.[4] From the reaction of CF3CF=CF2 and SO2F2 another sulfonate is easily generated.[5] A fluorinated diol enables us to prepare a new cyclic carbonate.[6] Surprisingly enough we found a versatile overcharge preventing additive in a nitrogen containing-heterocyclic carbene-PF5 adduct.[7-9]. Further derivatives were synthesized, preparative details discussed and some electrochemical features disclosed.

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[1] J. Power Sources, 2012, 205, 408-413.
[2] EP 2011/001025, WO2012084066 (A1).
[3] DE 102011052156 A1, WO 2013/014180 A1.
[4] DE 10 2012 105 377.4.
[5] DE 10 2012 101 670.4,  PCT/EP2013/053949.
[6] DE 10 2012 104 567.4.
[7] Organometallics, 2012, 31, 1278–1280.
[8] J. Electrochem. Soc., 2012, 15849, A1587-A1590.
[9] DE 10 2011 055 028.3, PCT/EP2012/071544.

## FMEC11.3

# Single-ion BAB triblock copolymers as efficient solid electrolytes for lithium metal batteries

**R. BOUCHET** [(a)]*, **A. ABOULAICH** [(a)], **S. MARIA** [(b)], **R. MEZIANE** [(c)], **J.P. BONNET** [(c)], **M. ARMAND** [(c)], **L. LIENAFA** [(b)], **T.N.T. PHAN** [(b)], **D. BERTIN** [(b)], **D. GIGMES** [(b)], **R. DENOYEL** [(a)]

[(a)] LABORATOIRE MADIREL - UMR 7246, AIX-MARSEILLE UNIVERSITÉ - CNRS - MARSEILLE (FRANCE)
[(b)] Institut de Chimie Radicalaire - UMR 7273, AIX-MARSEILLE UNIVERSITÉ - CNRS - MARSEILLE (FRANCE)
[(c)] LRCS - UMR 7314, Université de Picardie Jules Verne - AMIENS (FRANCE)

* renaud.bouchet@univ-amu.fr

Today the environment is a major society concern and the polluting fossil energy consumption, more and more expensive, is a drag on our economy, thereby the development of alternative transportation such as electric or hybrid vehicles, has become a key need for a sustainable long term development[1]. The increase of energy density necessary to promote this future revolution imposes to develop “new” chemistries for both the active electrode materials and electrolyte[2]. The lithium metal as anode becomes the latest flavour for tomorrows’ battery based notably on Li-S and Li-air systems[3]. However, the use of lithium metal in batteries based on liquid electrolyte led unfortunately to safety problems associated to the formation of irregular metallic lithium electrodeposits during the recharge, which results in dendrite formation responsible for explosion hazards. The use of a solid polymer electrolyte (SPE) could solve most of the safety issues encounter with liquid electrolyte. However, the development of SPE has been hampered by two hurdles i/ the inability to design a SPE that has both a high ionic conductivity and good mechanical properties and ii/ the motions of lithium ions carry only a small fraction of the overall ionic current which leads during battery operation to the formation of strong concentration gradient with highly noxious effects like favored dendritic growth[4] and limited energy density especially when power increases.

Here we describe the physico-chemical and electrochemical properties of a new single-ion polymer electrolyte based on self-assembled polyanionic triblock copolymers BAB in order to finely tune the mechanical properties as well as the ionic conductivity and lithium transport number. The B block is a polyanionic polymer based on Poly(styrene trifluoromethanesulfonylimide of lithium) P(STFSILi) associated with a central A block based on a linear Poly(ethylene oxide) PEO. The single-ion conductivity is almost one order of magnitude higher than that of the state of the art for such materials ($1.310^{-5}$ $Scm^{-1}$ at 60°C) combined with a mechanical strength drastically improved. The electrochemical window stability is extended to more than 5 V. Battery prototypes have been assembled using a cathode formulated with $LiFePO_4$ as active material. The battery tests show that the power performances and cycling are outstanding particularly at 60°C which makes these materials highly attractive for next battery generation[5].

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[1] J. Tollefson, Nature, 456, 2008, 436-440
[2] F. Cheng, J. Liang, Z. Tao, J. Chen, Advanced Materials, 23, 2011, 1695-1715
[3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J-M. Tarascon, Nature Materials, 11, 2012, 19-29
[4] J-N Chazalviel, Physical Review A, 42, 1990, 7355-7367
[5] R. Bouchet et al., Nature Materials, 12, 2013, 452–457

## IL-FMEC12

# Advanced next generation high energy lithium battery

**K. AMINE** [(a)]*, **H. WU** [(a)], **Z. CHEN** [(a)], **I. BELHAROUAK** [(a)], **Z. ZHANG** [(a)], **W. WEI** [(a)], **J. YANG** [(a)], **A. ABOUIMRANE** [(a)], **Y.K. SUN** [(a)]

[(a)] Chemical Sciences & Engineering Division, Argonne National Laboratory - ARGONNE (USA)

* amine@anl.gov

To achieve a long electric drive range, new battery systems with advanced high capacity cathode and anode is needed. $xLi_2MnO_3\bullet(1\text{-}x)LiMO_2$ (M = Mn, Ni) cathode offers the potential of very high energy that can meet the PHEV 40 miles. Since this material operates at 4.6V, there is a need to stabilize the electrode-electrolyte interface to prevent surface reactivity and electrolyte oxidation at high voltage and high temperature in order to increase both cycle and calendar life. Our approach is to apply several advanced coating process that allow for coating fluoride based nano film at the positive active powder or at the electrode after processing. This coating improves significantly the life of the battery. We will also discuss another high energy cathode approach based of full gradient concentration at the particle level. In addition and in order to increase the energy density of the battery and enable high voltage electrolyte, Fluorine based electrolyte with high voltage capability will discuss.

# POSTER SESSION 1

## MONDAY, JULY 22

# Monday, July 22

# POSTER SESSION 1

**P1.1** **EXPANDING THE CHEMICAL SPACE OF FLUORINATED CYCLIC ALIPHATIC AMINES.**
**P. Mykhailiuk***, A. Artamonov, A. Shcherbatyuk, V. Yarmolchuk, A. Tkachenko, D. Radchenko, B. Chalyk, I. Kondratov, N. Tolmacheva, I. Komarov, A. Tolmachev
**Enamine Ltd, Chemistry, Kyiv (Ukraine)*

**P1.2** **SYNTHESIS OF NEW FLUORINATED CYCLOPROPYL AMINO ACID ANALOGUES**
**P. Jubault***, G. Milanole, J.-F. Bonfanti, S. Couve-Bonnaire, X. Pannecoucke
**INSA de Rouen, UMR 6014 COBRA, Mont-Saint-Aignan (France)*

**P1.3** **LIGAND PROMOTED ASYMMETRIC SYNTHESIS OF α-BROMO- α -FLUORO-β-LACTAM AND α, α -DIFLUORO- β -LACTAM**
**A. Tarui***, T. Ikebata, A. Tahira, K. Sato, M. Omote, A. Ando,
*Setsunan University, Pharmaceutical Chemistry, Hirakata (Japan)*

**P1.4** **NOVEL MIXED 3-(2,2,2-TRIFLUOROETHYL) AMINOQUINOLINE G-LACTAMS: DESIGN, SYNTHESIS AND FIRST BIOLOGICAL EVALUATION AS ANTIMALARIAL AGENTS**
D. Cornut, H. Lemoine, S. Kanishchev, A. Bienvenu, S. Picot, F. Albrieux, M. Médebielle, **J.-P. Bouillon***
**Université de Rouen, UMR CNRS 6014 COBRA, Mont-Saint- Aignan (France)*

**P1.5** **THE SYNTHESIS AND CHARACTERISATION OF MULTI-VICINAL FLUOROCYCLOHEXANES AS POLAR ORGANIC MOTIFS**
**N. Keddie***, D. O'Hagan
**University of St Andrews, School of Chemistry, St Andrews (UK)*

**P1.6** **SYNTHESIS OF BIOLOGICALLY ACTIVE α-TFM-PROLINE CONTAINING PEPTIDES**
**G. Chaume***, J. Simon, L. Astasidi, I. Jlalia, , E. Dzhambazova, R. Hadjiolova, E. Chelain, J. Pytkowicz, N. Lensen, A. Bocheva, T. Brigaud
**Université de Cergy-Pontoise, Laboratoire SOSCO, Cergy-Pontoise (France)*

**P1.7** **CHALLENGING RESULT OF NEW β-ALKOXYVINYL TRIFLUOROMETHYL KETONES SYNTHESIS**
**I. Gerus*,** Y.I. Zhuk, G.V. Röschenthaler
*Institute of Bioorganic Chemistry & Petrochemistry, NAS, Kyiv (Ukraine)*

**P1.8** **A NEW LIFE FOR AN OLD REAGENT: FLUOROALKYL AMINO REAGENTS (FAR) AS AN EFFICIENT TOOL FOR THE SYNTHESIS OF DIVERSELY FLUORINATED PYRAZOLES**
F. Giornal, **G. Landelle*,** S. Pazenok, N. Lui, J.-P. Vors, F. Leroux,
**Université de Strasbourg, Laboratoire de Chimie Moléculaire, Strasbourg (France)*

**P1.9** DIFLUOROMETHYLBENZOXAZOLE PYRIMIDINE THIOETHER (DFMB) DERIVATIVES AS NOVEL NON-NUCLEOSIDE HIV-1 REVERSE TRANSCRIPTASE INHIBITORS
J. Boyer, A. Menot, R. Terreux, E. Arnoult, J. Unge, D. Jochmans, J. Guillemont, **M. Médebielle***
**Université Claude-Bernard Lyon 1, ICBMS UMR 5246, Villeurbanne (France)*

**P1.10** TRIFLUOROMETHYL-DERIVED PYRIDO[3,2-d]PYRIMIDINE DERIVATIVES FROM PURINES: SYNTHESIS AND ANTIMALARIAL ACTIVITIES
B. Ovadia, R. Steyaert, A. Faurie, N. Chopin, T. Guerin, S. Picot, A. Lavoignat, B. Joseph, **M. Médebielle***
**Université Claude-Bernard Lyon 1, ICBMS UMR 5246, Villeurbanne (France)*

**P1.11** SOME NEW APPLICATIONS OF FLUORINE - DERIVED REAGENTS IN ORGANIC CHEMISTRY
**J. Gatenyo***, I. Vints, S. Rozen
**Tel Aviv University, Organic Chemistry, Tel Aviv (Israël)*

**P1.12** SYNTHETIC APPROACH TO NEW DIFLUOROMETHELENE CONTAINING AMINES
G. Posternak, **I. Kondratov***, N. Tolmacheva, A. Tolmachev, K. Tarasenko, O. Hilchevsky
**Enamine Ltd, Chemistry, Kyiv (Ukraine)*

**P1.13** SYNTHESIS AND EVALUATION OF FLUORINATED ANALOGUES OF S1P ANTAGONISTS
**V. Pushpa Prasad***, P. Keul, L. Bodo, M. Schäfers, G. Haufe
**Institute of Organic Chemistry Münster University Münster (Germany)*

**P1.14** SYNTHESIS OF TRIFLUOROMETHYLATED PYRROLES
**T. Billard***, O. Marrec, B. Langlois, J.-P. Vors, S. Pazenok
**Université Claude-Bernard Lyon I, Laboratoire Surcoof, Villeurbanne (France)*

**P1.15** ELECTROPHILIC TRIFLUOROMETHANESULFENYLATION OF NUCLEOPHILIC SPECIES WITH TRIFLUOROMETHANESULFENAMIDES
**S. Alazet***, F. Baert, J. Colomb, T. Billard
**Université Claude-Bernard Lyon I, Laboratoire Surcoof, Villeurbanne (France)*

**P1.16** SYNTHESIS OF FLUORINATED EXO-GLYCALS AS A POTENT GLYCOSIDASES INHIBITOR VIA MODIFIED JULIA REACTION
S. Habib, F. Larnaud, E. Pfund, **T. Lequeux*,** C. Ortiz Mellet, T. Mena, P. G. Goekjian, D. Gueyrard,
**University of Caen, LCMT, Caen (France)*

**P1.17** BIS[PENTAKIS(TRIFLUOROMETHYL)PHENYL]AMINE AND ITS DERIVATIVES
**A. Kütt***, I. A. Koppel
**University of Tartu, Institute of Chemistry, Tartu (Estonia)*

### P1.18 $CF_3$ LABELED SUBSTRATE OF 20S PROTEASOME TO MEASURE $IC_{50}$ OF PROTEASOME INHIBITORS BY $^{19}F$ NMR SPECTROSCOPY

**S. Ongeri***, M. Keita, J. Kaffy, E. Morvan, C. Troufflard, B. Crousse
**Université Paris-Sud, Molécules Fluorées & Chimie Médicinale, UMR CNRS 8076, Labex Lermit, Châtenay-Malabry (France)*

### P1.19 APPLICATION OF SKRAUP REACTION FOR SYNTHESIS OF NOVEL FLUORINATED PHENANTHROLINES

**C. Lüdtke***, A. Haupt, N. Kulak
**FU Berlin, Inorganic Chemistry, Berlin (Germany)*

### P1.20 SYNTHESIS OF OPTICALLY PURE 2-DIFLUOROMETHYL AZIRIDINE

**S. Hiramatsu**
*Okoyama University, Hetero Atom Chemistry, Okayama (Japan)*

### P1.21 PROTONATION OF MALONIC ACID: PREPARATION AND CHARACTERIZATION OF THE MONO - AND DIPROTONATED MALONIC ACID

**M. Schickinger*,** K. Lux, A. Kornath,
**Ludwig-Maximilian University, Dept. of Chemistry, Munich (Germany)*

### P1.22 SYNTHESIS OF FLUORINATED α-GALACTOSYLCERAMIDE

**N. Van Hijfte***, S. Colombel, T. Poisson, E. Leclerc, X. Pannecoucke*,*IRCOF - INSA de Rouen, UMR 6014 COBRA, Mont-Saint-Aignan (France)*

### P1.23 FLUOROALKYLATION OF 5, 10, 15 - TRIS(PENTAFLUOROPHENYL) CORROLE

**R. Du*,** Q. Chen, J.C. Xiao
**Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai (China)*

### P1.24 FLUORINATED BUILDING BLOCKS FOR HYALURONIC ACID SUBUNITS SYNTHESIS

K. Koroniak-Szejn**, M. Bardzinski*, J. Jurek***
*Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

### P1.25 PREPARATION AND CHARACTERISATION OF NOVEL α-FLUORINATED-GAMMA-AMINOPHOSPHONATE OXALATES

**M. Kazmierczak***, G. Dutkiewicz, M. Kubicki, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

### P1.26 SYNTHESIS OF (α,α-DIFLUOROPROPARGYL) PHOSPHONATES VIA ALDEHYDE-TO-ALKYNE HOMOLOGATION

**R. Pajkert*,** G.-V. Roeschenthaler,
**Jacobs University Bremen GGMBH, Scholl of Engineering & Science, Bremen (Germany)*

### P1.27 CONSTRUCTION OF SELECTED HETEROCYCLES WITH PER- AND POLYFLUOROALKOXY GROUPS BASED ON ALIPHATIC PRECURSORS

Y. Davydova, **T. Sokolenko***, Y. Yagupolskii,
**Institute of Organic Chemistry, NAS of Ukraine, Dept. of Organofluorine compounds, Kyiv (Ukraine)*

### P1.28 Synthesis of trifluoromethylated γ-aminophosphonates by nucleophilic aziridine ring opening

**T. Cytlak***, M. Saweliew, G Dutkiewicz, M. Kubicki, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

### P1.29 Synthesis of fluorinated structural analogues of FTY 720 (Gilenya®) and sphingosine-1-phosphate

**R. Shaikh*,** S. Schilson, P. Keul, L. Bodo, M. Schäfers, G. Haufe
**Universität Münster, Organisch-Chemisches Institut Münster (Germany)*

### P1.30 The 1, 3-dipolar cycloaddition route to fluorinated nucleoside analogues

**H. Wójtowicz-Rajchel***, E. Muszynska, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

### P1.31 Synthesis and ring opening of α-monofluorinated β- & γ-epoxy phosphonate derivatives

**M. Rapp***, A. Witkowska, K. Margas, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Poznan (Poland)*

### P1.32 Exploring the chemical nature of Meerwein' s catalytic active BF$_3$ - carboxylic acid adducts

**S. Parizek*,** W. Frank
*Henrich-Heine Institut für Anorganische Chemie Düsseldorf, (Germany)*

### P1.33 Synthesis and application of fluorinated β-iminophosphonates derivatives

**M. Szewczyk***, M. Rapp, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Dept of Synthesis & structure of organic compounds, Poznan (Poland)*

### P1.34 Synthesis of trifluoromethylated tripeptides and evaluation of their hydrophobicity

**E. Devillers*,** J. Pytkowicz, E. Chelain, V. Gasparik, T. Brigaud,
**Université de Cergy-Pontoise, Laboratoire SOSCO, Cergy-Pontoise (France)*

### P1.35 Enantioselective Transfer Hydrogenation of CF3-substituted Ketimines by Means of Chiral Phosphoric Acid

**T. Akiyama**
*Gakushuin University, Department of Chemistry, Tokyo (Japan)*

### P1.36 Hydrophobicity and Helix-propensity of fluorinated isoleucine variants

**S. Huhmann***, H. Erdbrink, E. Nyakatura, U. Gerling, C. Czekelius, B. Koksch,
**FU Berlin, Institute of Chemistry & Biochemistry, Berlin (Germany)*

### P1.37 The electrophilic fluoroalkylation of Ni(II) N-Confused porphyrins with fluoroalkylarylsulfonium salts

**G. Zong***, F. Hao, H. W. Jiang, Z. Zhou, R. Du, Q. Chen, J.-C. Xiao
**Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, Chinese Academy of Sciences, Shanghai (China)*

**P1.38** **STRATEGIC APPROACH TO SYNTHESIS OF 2, 3, 5, 6-(TETRAKIS)TRIFLUOROMETHYL-4-CHLORO PYRIDINE AND ITS DERIVATIVES**
S. Sergeev, **V. Petrik***,
**Chemtaurus GmbH, Bremen (Germany)*

**P1.39** **ORGANOCATALYTIC REACTIONS OF α-TRIFLUOROMETHYLATED COMPOUNDS WITH ALKENES**
Q. Wang, F. Huan, C. Xiao, ~~J.~~ M. Gao, X. Yang, S. I .Murahashi, Q. Chen, **Y. Guo***,
**Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai (China)*

**P1.40** **TUNING THE REACTIVITY OF DIFLUOROMETHYL SULFOXIMINES FROM ELECTROPHILIC TO NUCLEOPHILIC: STEREOSELECTIVE NUCLEOPHILIC DIFLUOROMETHYLATION OF ARYL KETONES**
X. Shen, **W. Zhang***, C. Ni, J. Hu
**Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai (China)*

**P1.41** **SYNTHESIS OF MONO-FLUORINATED CYCLOPROPANES AND AZIRIDINES USING α-(FLUOROVINYL) DIPHENYLSULFONIUM SALT**
**K. Hirotaki***, T. Hanamoto
**Saga University, Dept of Chemistry & Applied Chemistry, Saga (Japan)*

**P1.42** **SYNTHESIS OF NEW [18F]FLUORO SUGAR PROSTHETIC GROUPS TO RADIOLABELLED PEPTIDE FOR PET IMAGING**
**S. Lamande-Langle***, C. Collet, R. Hensienne, F. Chrétien, F. Maskali, P.-Y. Marie, G. Karcher, Y. Chapleur
**Université de Lorraine - CNRS, UMR 7565 SRSMC, Vandoeuvre- Les- Nancy (France)*

**P1.43** **ASSESSMENT OF THE POTENTIAL OF THE FLUORIDE AND CHLORIDE SALTS FOR CSP**
**B. Kubikova***, N. Pfleger, T. Bauer
**Institute of Inorganic Chemistry, Dept of Molten Salts, Bratislava (Slovakia)*

**P1.44** **VERSATILE PREPARATIONS OF PERFLUOROALKYLATED BIS-SULFILIMINES AND BIS-SULFOXIMINES**
**B. Pegot***, C. Urban, P. Diter, E. Magnier
**Université de Versailles-Saint-Quentin-CNRS, UMR 8180, Versailles (France)*

**P1.45** **AN IMPROVED SYNTHESIS OF THE 2, 3, 4-TRIDEOXY-2, 3, 4-TRIFLUORO HEXOSE ANALOGUE OF D-GLUCOSE**
**M. Corr***, D. O'Hagan
**University of St Andrews, Biomolecular Sciences Research Complex, St Andrews (UK)*

**P1.46** **EXTENDING THE SYNTHETIC UTILITY OF THE FLUORINASE FOR POSITRON EMISSION TOMOGRAPHY USING CLICK CHEMISTRY**
**S. Thompson*,** S. McMahon, C. Dreher, J. Naismith, D. O'Hagan,

**University of St Andrews, Biomolecular Sciences Research Complex, St Andrews (UK)*

**P1.47** DIRECT ELECTROPHILIC TRIFLUOROMETHYLATION OF NITROGEN CONTAINING ARENES USING A HYPERVALENT IODINE REAGENT
**N. Frueh***, A. Togni
**ETH Zürich, Laboratory of Inorganic Chemistry, Zurich (Switzer land)*

**P1.48** INVESTIGATIONS ON ACTIVATED HYPERVALENT IODINE TRIFLUOROMETHYLATION REAGENTS
**E. Otth***, A. Togni
**ETH Zürich, Laboratory of Inorganic Chemistry, Zurich (Switzer land)*

**P1.49** SYNTHESIS OF *SYN*-HEXAFLUOROALKANE
**N. Al-Maharik***
**University of St Andrews, Biomolecular Sciences Research Complex, St Andrews (UK)*

**P1.50** CLAISEN REARRANGEMENT OF FLUORINATED ALLYL-VINYL ETHERS
**B. Marciniak***, M. Rapp, H. Koroniak
**Adam Mickiewicz University, Faculty of Chemistry, Dept of Synthesis & structure of organic compounds, Poznan (Poland)*

**P1.51** ION MOBILITY AND PHASE TRANSITIONS IN CRYSTAL PHASES OF HEPTAFLUORODIANTIMONATES $MSb_2F_7$ ($M = K, Cs, NH_4$) AND $Cs_{(1-x)}M'_xSb_2F_7$ ($M' = K, NH_4$) ACCORDING TO NMR AND DSC DATA
**V. Kavun***, L. Zemnukhova, M. Polyantsev, V. Kharchenko
**Institute of Chemistry, FEB RAS, NMR LAB., Vladivostok (Russia)*

**P1.52** SYNTHESIS AND CHARACTERISATION OF NANOSCOPIC $SrF_2$ VIA SOL-GEL SYNTHESIS
**L. Schmidt*,** E. Kemnitz
**Humboldt-Universität zu Berlin, Dept of Chemistry, Berlin (Germany)*

**P1.53** MASS-SPECTROMETRIC STUDY ON THE OCCURRENCE OF ELEMENTAL FLUORINE IN THE NATURAL MINERAL «ANTOZONITE»
P.P. Semyannikov, **V. Mitkin***, F. Kraus, S.V. Trubin
**Nikolaev Institute of Inorganic Chemistry, SB RAS, Lab of Carbon Materials Chemistry, Novosibirsk (Russia)*

**P1.54** X-RAY PHOTOELECTRON SPECTROSCOPY OF INORGANIC FLUORIDES
**M. Boca**
*Institute of Inorganic Chemistry, FEB RAS, Dept of Molten Salts, Bratislava (Slovakia)*

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**Tomsk Polytechnic University, Fluorine Chemistry & Engineering, Tomsk (Russia)*

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A. Sloboduyk, N. Didenko, **V. Kavun***
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_Kirensky Institute of Physics, Crystalphysics Lab, SB RAS, Krasnoyarsk (Russia)_

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_*Prokhorov General Physics Institute, RAS, Laser Materials & Technology Research Center, Moscow (Russia)_

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_*Institut de Chimie de Clermont-Ferrand, Equipe Matériaux Inorganiques, Clermont-Ferrand (France)_

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**Organisch-Chemisches Institut, Universität Münster, Münster (Germany)*

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**Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk (Russia)*

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**A. Dyachenko***, R. Kraydenko, A. Kiselev
**Tomsk Polytechnic University, Department of Rare, Scattered and Radioactive Element Technology, Tomsk (Russia)*

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*ICMCB-CNRS, Pessac (France)*

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**ENSCP-Chimie ParisTech, LMCP UMR 7574–CAES, Paris (France)*

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**Central Glass Co., ltd., Chemical Research Center, Ube (Japan)*

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**Institut Charles Gerhardt, IAM-ENSCM, Montpellier (France)***)**

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**D.-S. Shin*,** B.V.D. Vijaykumar
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**Università degli Studi di Padova, Lab Sulla Chimica del Fluoro, Padova (Italy)*

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**University of Pretoria, Dept. of Chemical Engineering, Pretoria (South Africa)*

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**Institut Charles Gerhardt, IAM-ENSCM, Montpellier (France)*

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**Solvay Specialty Polymers, Bollate (Italy)*

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**Politecnico di Milano, Fluoritech, Milano (Italy)*

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**J.-M Vincent***, G. Raffy, A. Del Guerzo, A. Motreff, C. Belin
** CNRS-Université de Bordeaux, ISM, Talence (France)*

**P1.83** **SURFACTANTS WITH LOW FLUORINE CONTENT**
J. El Maiss, **M. Wolfs***, E. Taffin De Givenchy, F. Guittard,
**Université de Nice Sophia Antipolis & CNRS, LPMC - UMR 7336, Nice (France)*

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**Université de Nice Sophia Antipolis & CNRS, LPMC - UMR 7336, Nice (France)*

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**W. Ma***, Y. Higaki, A. Takahara
**Kyushu University, WPI-I2CNER, Fukuoka (Japan)*

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P. Crouse, **P. Sonnendecker***
**University of Pretoria, Dept. of Chemical Engineering, Pretoria (South Africa)*

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**G. Marchionni**, S. Petricci, S. Barbieri, C. Tonelli
*Solvay Specialty Polymers Italy Spa, Basic Fluorine Chemistry R&D Area Manager, Bollate (Italy)*

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I. Bolbukh, P. Kuzema, B. Mischanchuk, V. Tertykh, E. Durand , **A. Tressaud***
**ICMCB – CNRS, Pessac (France) and Institute of Surface Chemistry, NASU, Kyiv (Ukraine)*

## P1.1

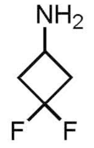
# Expanding the chemical space of fluorinated cyclic aliphatic amines.

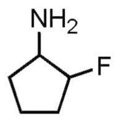
**P. MYKHAILIUK** [a]*, **A. ARTAMONOV** [a], **A. SHCHERBATYUK** [a], **V. YARMOLCHUK** [a], **A. TKACHENKO** [a], **D. RADCHENKO** [a], **B. CHALYK** [a], **I. KONDRATOV** [b], **N. TOLMACHEVA** [a], **I. KOMAROV** [a], **A. TOLMACHEV** [a]
[a] ENAMINE LTD, CHEMISTRY - KYIV (UKRAINE)
[b] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)
* Pavel.Mykhailiuk@mail.enamine.net

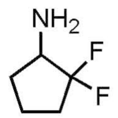
Modern drug discovery is hard to imagine without fluorine, as ~20% of all pharmaceuticals contain this element. To date, however, only small part of the theoretically possible chemical space is covered. Many simple combinations of fluorine with carbon and nitrogen atoms are still unknown, constraining thereby the probability to find new drugs that could benefit from a well-placed fluorine group.

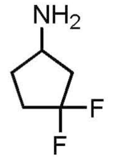
Reduced molecular flexibility and enhanced number of $sp^3$-carbons have been suggested as the distinguishing features of approved drugs. Implementation of these principles leads to conceptually attractive space for drug discovery: fluorinated cyclic aliphatic motif.

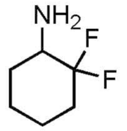
In this work, the chemical space covered by fluorinated cyclic aliphatic amines (FCAAs) was explored [1-5]. The possible origin for the rare occurrence of FCCA-motif in drug discovery was the following: the known FCAAs constituted only tiny fraction among all theoretically possible structures. Therefore, a library of novel FCAAs was synthesized. Commercial availability of the obtained products has led to great interest from top pharmaceutical companies.

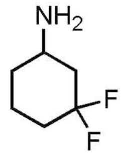


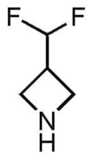


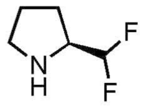


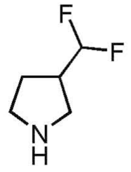


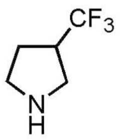


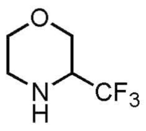


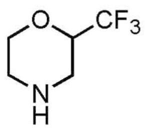


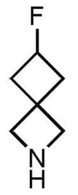


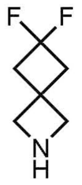


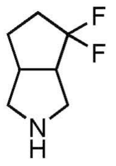


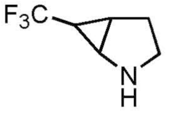


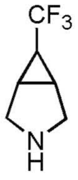


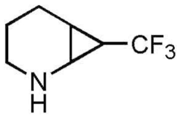












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## P1.2

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# Synthesis of new fluorinated cyclopropyl amino acid analogues

**P. JUBAULT** [(a)]*, **G. MILANOLE** [(a)], **J. BONFANTI** [(b)], **S. COUVE-BONNAIRE** [(a)], **X. PANNECOUCKE** [(c)]

[(a)] INSA DE ROUEN, UMR 6014 COBRA - MONT SAINT-AIGNAN (FRANCE)
[(b)] Janssen-Cilag, Campus de Maigremont - VAL DE REUIL (FRANCE)
[(c)] IRCOF - INSA de Rouen, UMR 6014 COBRA - MONT SAINT-AIGNAN (FRANCE)

* philippe.jubault@insa-rouen.fr

Synthesis of biologically active peptides is a central goal in medicinal chemistry. However, major drawbacks in this area are their low metabolic stability and poor ligand-receptor interactions eroding the bioavailability of peptide-based drugs. To overcome these disadvantages, considerable interest has been devoted to synthesize peptidomimetics by modifying the natural sequence of amino acids of bioactive peptides. In our ongoing project, we decided to focus on the design of peptidomimetics including a fluorinated cyclopropane moiety. Incorporation of a three-membered ring influences the secondary structure, leading to conformationally constrained peptide chains[1]. Thus, the ligand affinity for the enzyme binding site would be improved, as well as the orientation of amino acid side chains. Moreover, many studies show that the presence of a fluorine atom induces modifications of various parameters (lipophilicity, acidity/basicity, electronic distribution or bond lengths [2]. We report here the efficient synthesis of fluorinated cyclopropyl analogs of four natural amino acids (methionine, leucine, arginine and lysine), and the incorporation of these scaffolds in peptides. We also reported the asymmetric synthesis of the leucine analog[3] as well as the synthesis of fluorinated analog of TMC 435 (which incorporates within its structure a cyclopropyl amino-acid unit), a potent NS3/4A serine protease inhibitor for HCV treatment.

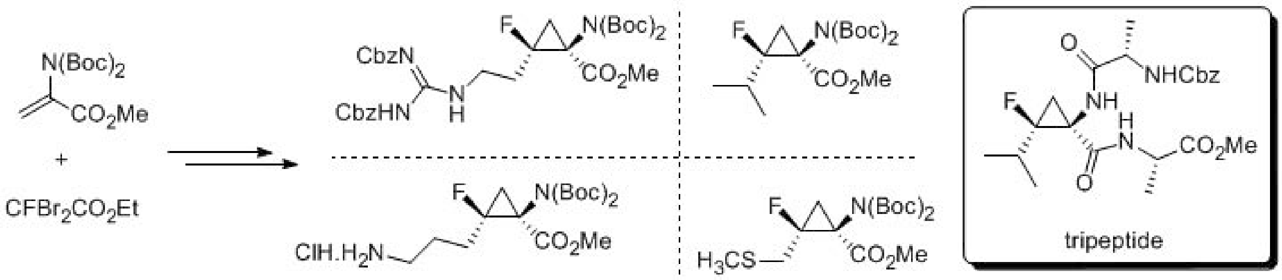

*Figure 1. Access to fluorinated cyclopropyl peptidomimetics*

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## P1.3

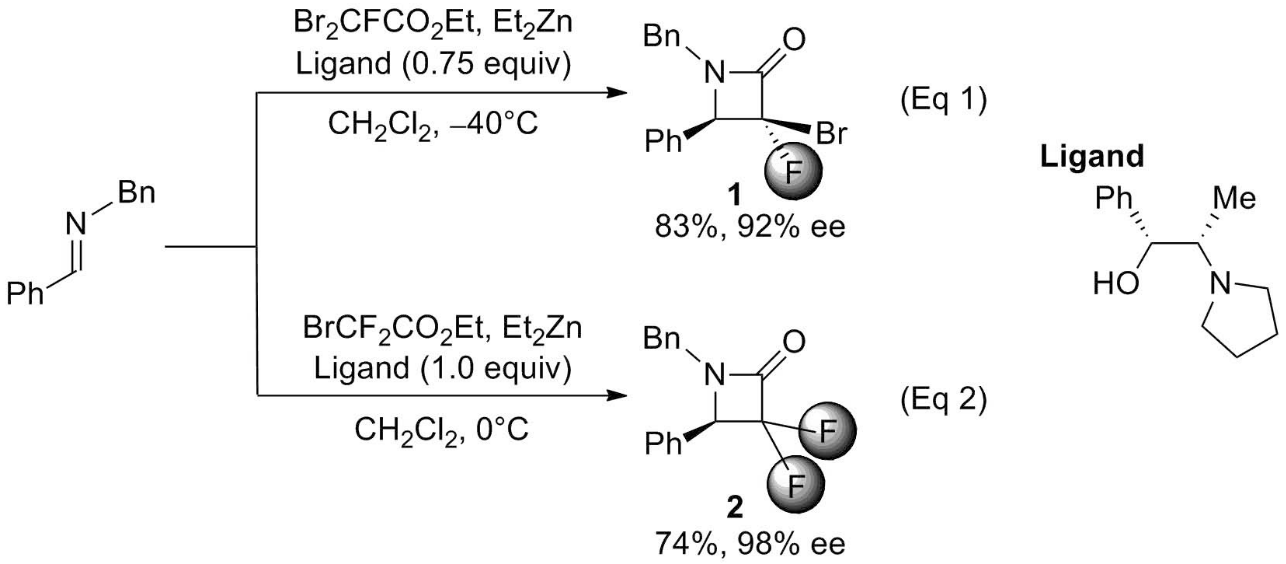
# Ligand promoted asymmetric synthesis of α-bromo-α-fluoro-β-lactam and α,α-difluoro-β-lactam

**A. TARUI** [(a)]*, **T. IKEBATA** [(a)], **A. TAHIRA** [(a)], **K. SATO** [(a)], **M. OMOTE** [(a)], **A. ANDO** [(a)]

[(a)] FACULTY OF PHARMACEUTICAL SCIENCES, SETSUNAN UNIVERSITY, LABORATORY OF PHARMACEUTICAL CHEMISTRY - HIRAKATA (JAPAN)

* tarui-a@pharm.setsunan.ac.jp

An introduction of fluorine atoms gives the unique property to organic molecules, which enhance its lipophilicity and chemical stability. These features are useful for medicinal and agrochemical productions. In order to utilize the above features, it is important not only to introduce a fluorine substituent but also to synthesize a chiral fluorine compound. Recently, we reported diastereoselective synthesis of α-bromo-α-fluoro-β-lactam (1) and synthesis of α,α-difluoro-β-lactam (2) using Reformatky-type reaction.[1] To expand our investigations, we focused on the asymmetric synthesis of these fluorinated β-lactams. The reaction condition followed the recent papers reported by Stuart and co-workers.[2] Consequently, the reaction of ethyl dibromofluoroacetate with *N*-benzylidenebenzylamine using $Et_2Zn$ in the presence of the aminoalcohol ligand gave the desired product 1 diastereo- and enantioselectively (eq 1). Furthermore, the reaction of ethyl bromodifluoroacetate, instead of ethyl dibromofluoroacetate, gave the corresponding product 2 with high enantioselectivity (eq 2). These results are the first example for the ligand promoted asymmetric imino-Reformatsky reaction of fluorine-containing haloesters. We will discuss the details of this topics.



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## P1.4

# Novel mixed 3-(2,2,2-trifluoroethyl) aminoquinoline g-lactams: design, synthesis and first biological evaluation as antimalarial agents

**D. CORNUT** [(a)(b)], **H. LEMOINE** [(a)(b)], **S. KANISHCHEV** [(a)], **A. BIENVENU** [(b)(c)], **S. PICOT** [(b)(c)], **F. ALBRIEUX** [(d)], **M. MÉDEBIELLE** [(b)*], **J. BOUILLON** [(a)*]

[(a)] UNIVERSITÉ DE ROUEN, Chimie Organique Bioorganique Réactivité et Analyses (COBRA), IRCOF, UMR CNRS 6014 - MONT SAINT AIGNAN (FRANCE)
[(b)] Institut de Chimie et Biochimie Moléculaire et Supramoléculaire (ICBMS), UMR 5246, Equipe « Synthèse de Molécules d'Intérêt Thérapeutique (SMITH) », UMR CNRS – UCBL – INSA 5246 - VILLEURBANNE (FRANCE)
[(c)] Université Claude Bernard Lyon 1, Malaria Research Unit (MRU), Faculté de Médecine - LYON (FRANCE)
[(d)] Université Claude Bernard Lyon 1, Centre Commun de Spectrométrie de Masse (CCSM) et Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS) - VILLEURBANNE (FRANCE)

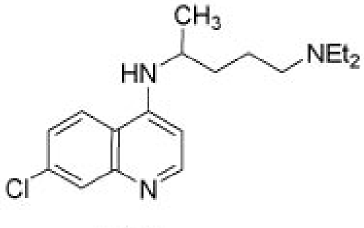
* jean-philippe.bouillon@univ-rouen.fr
maurice.medebielle@univ-lyon1.fr

Malaria is an infectious disease that affects approximately 300 million people annually, causing about one million deaths (mostly young children). It is most common in tropical and subtropical areas and 90% of all cases are found in sub-Saharan Africa. The widespread resistance of many *P. falciparum* strains to most readily available drugs, especially to Chloroquine (CQ, 1), hinders malaria control and is therefore a major public health problem.

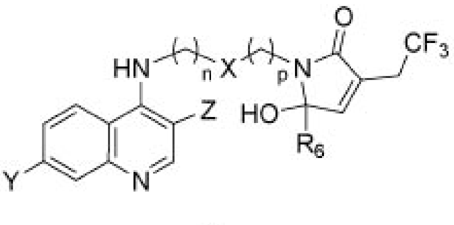
Recently, we have initiated a research program dedicated to synthesis of two series of 3-(2,2,2-fluoroethyl)-g-lactams derived from 4-aminoquinoline in order to discover new drug candidates for malaria treatment. The structures 2 and 3 were prepared in several steps with good overall yields, starting from g-ketothioesters or g-lactones as fluorinated building blocks and 4-aminoquinoline-derived amine reagents.

Several g-lactam derivatives were identified as very potent compounds with *in vitro* activity against *P. falciparum* clones of variable sensitivity (CQ-Sensitive 3D7 and CQ-Resistant W2 strains) in the range of 19 to 50 nM. Our biological data indicate also that the most potent structures are not cytotoxic up to 100 µM (HUVEC cells) with good resistance indexes (close to 1.0-2.5) [1].

*This work was supported by ANR Emergence 2011 (ANR-11-EMMA-04-QUINOLAC).*



CQ: 1



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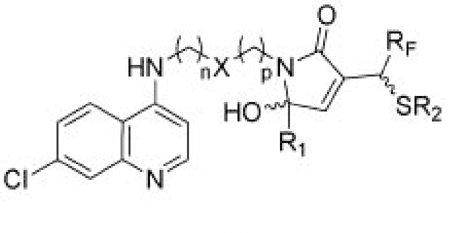

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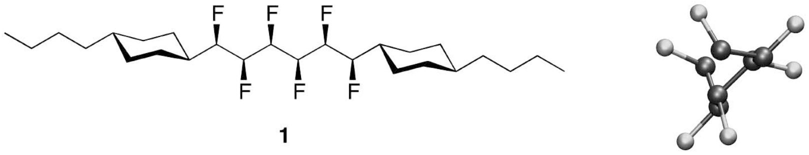
**P1.5**

# The synthesis and characterisation of multi-vicinal fluorocyclohexanes as polar organic motifs

**N. KEDDIE** [(a)]*, **D. O'HAGAN** [(a)]

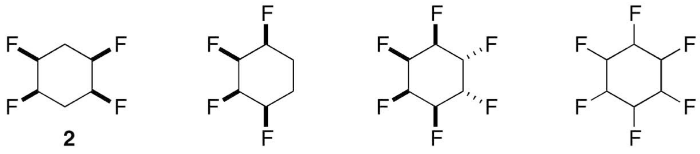
[(a)] Biomolecular Sciences Research Complex, University of St Andrews, SCHOOL OF CHEMISTRY - ST ANDREWS (UNITED KINGDOM)

* nsk@st-andrews.ac.uk



1

**Fig. 1** - Linear all-*syn* hexafluorohexane **1**, with edited crystal structure showing fluorine gauche interactions forming complete helical twist.



2 3 4 5

**Fig. 2** - Multivicinal fluorocyclohexane target molecules.

Previous research in our group has explored a new class of fluoroalkanes where C-F bonds are arranged adjacent to each other with specific stereochemistries. For example, the stereospecific installation of four to six multivicinal fluorine atoms in linear aliphatic systems was reported.[1] The all-*syn* arrangement of these fluorine atoms was a particular focus, with the hexafluoro alkane 1 forming a complete helical twist, owing to repulsion between four sets of C-F bonds that are 1,3 to each other (see Fig. 1). Such motifs have potential in materials applications eg. for liquid crystals, if dipoles can be maintained, however, the propensity towards helicity reduces the dipole moment of such all-*syn* linear systems.

Accordingly cyclic systems are a current focus,[2-4] where stereoisomers are designed such that there are two sets of C-F bond lying 1,3 to each other and both occupying axial orientations in the chair conformation, This induces a strong dipole, which cannot be compromised by helical twisting and thus these molecules are better prospects as polar organic motifs. A series of such compounds have been prepared as illustrated in Fig 2.

This presentation will describe recent progress in the synthesis of this class of molecules. Variable temperature NMR studies and solid-state characterisation of representatives of this class of molecules will also be presented.

## P1.6

# Synthesis of biologically active α-Tfm-proline containing peptides

**G. CHAUME [a]*, J. SIMON [a], L. ASTASIDI [b], I. JLALIA [a], E. DZHAMBAZOVA [b], R. HADJIOLOVA [c], E. CHELAIN [a], J. PYTKOWICZ [a], N. LENSEN [a], A. BOCHEVA [c], T. BRIGAUD [a]**

[a] UNIVERSITE DE CERGY-PONTOISE, LABORATOIRE SOSCO - CERGY-PONTOISE (FRANCE)
[b] Department of Physiology and Clinical Physiology, Faculty of Medicine, Sofia University - SOFIA (BULGARIA)
[c] Department of Pathophysiology, Faculty of Medicine, Medical University - SOFIA (BULGARIA)

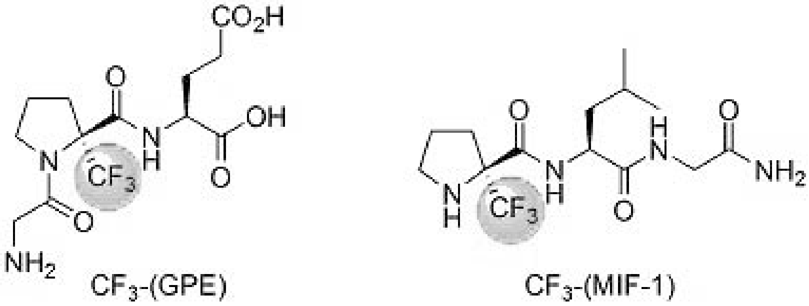
* gregory.chaume@u-cergy.fr

α-Trifluoromethyl α-amino acids (α-Tfm-AAs) are very attractive compounds since their incorporation into peptides can result in increased chemical and thermal stability, increased resistance to degradation by proteases, and enhanced hydrophobicity, giving better affinities for lipid membranes.[1] Moreover, they can induce stabilization of particular conformations and better auto-assembly.[2] Additionally, the trifluoromethyl group can serve as a label for various $^{19}F$ NMR studies.[3]

Unfortunately, this strategy is seriously limited by two main drawbacks: (1) there are very few synthetic methods available for their preparation in gram scale and in enantiopure form; (2) their incorporation into a peptide chain remains a challenge due to the lack of nucleophilicity of the α-Tfm-AAs amino group and the steric and electronic hindrance of the $CF_3$ group.

Our research group is interested in the preparation of enantiopure α-Tfm-AAs starting from chiral $CF_3$-oxazolidines (Fox)[4] and their incorporation in peptides of therapeutic interest in order to investigate the direct effect of the fluorinated amino acid on the biological activity.[5]

Here, we report the synthesis of two $CF_3$-proline containing analogues of biologically active tripeptides, the GPE (Gly-Pro-Glu) and the MIF-1 (Pro-Leu-Gly-NH2), respectively described for its potent neuroprotective activity during various CNS injuries and its analgesic effect on nociception during acute pain.[6]



*Structures of CF3-GPE and CF3-(MIF-1)*

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[1] (a) Salwiczek, M.; Nyakatura, E.K.; Gerling, U. I. M.; Ye, S.; Koksch B. *Chem. Soc. Rev.* **2012**, *41*, 2135-2171. (b) Merkel, L.; Budisa, N. *Org. Biomol. Chem.* **2012**, *10*, 7241-7261.

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[3] (a) Tkachenko, A.N.; Mykhailiuk, P. K.; Afonin, S.; Radchenko, D. S; Kubyshkin, V. S.; Ulrich, A.; Komarov, I. V. *Angew. Chem. Int. Ed.* **2013**, *52*, 1486-1489. (b) Takaoka, Y.; Kioi, Y.; Morito, A.; Otani, J.; Arita, K.; Ashihara, E.; Ariyoshi, M.; Tochio, H.; Shirakawa, M.; Hamachi, I. *Chem. Commun.* **2013**, *49*, 2801-2803.

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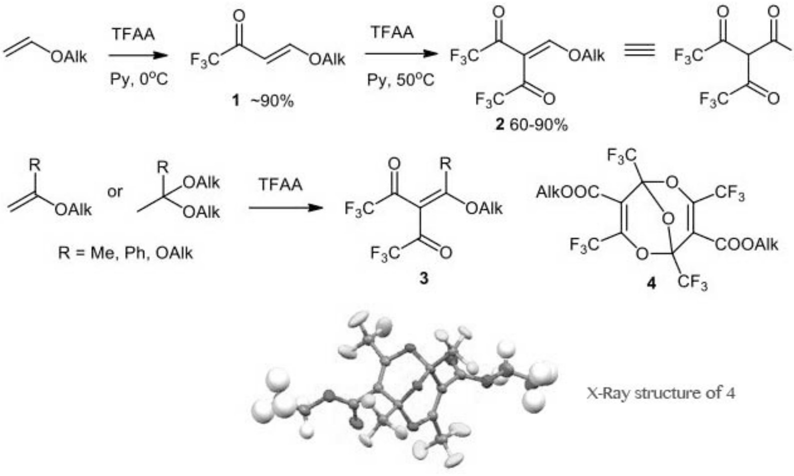
## P1.7

# Challenging Result of New β-Alkoxyvinyl Trifluoromethyl Ketones Synthesis

**I.I. GERUS** [(a)]*, **Y.I. ZHUK** [(a)], **G.V. RÖSCHENTHALER** [(b)]
[(a)] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)
[(b)] Jacobs University Bremen gGmbH, School of Engineering and Science - BREMEN (GERMANY)

* igerus@hotmail.com

The *mono*-trifluoroacetylation [1] of alkyl vinyl ethers is one of the prominence methods to synthesize readily available and versatile reactive β-alkoxyvinyl trifluoromethyl ketones 1 – widely used fluorinated building blocks [2]. Instead of this state only several articles have been published on the *bis*-trifluoroacetylation [3] of alkyl vinyl ethers in spite of higher reactivity of *bis*-trifluoroacetylated olefins 2 and interesting *bis*-trifluoromethyl containing products obtained from 2.



Therefore, we have studied the *bis*-polyfluoroacylation of various alkyl vinyl ethers bearing methyl, phenyl or alkoxy groups at α-position to alkoxy substituent in the starting olefins. The desirable products 3 are chemical equivalents of tricarbonylic compounds: triketones (R = Me, Ph) or diketoesters (R = OAlk), and they are of interest as perspective, previously unknown, fluorinated building blocks.

Unexpectedly, the reaction of trialkyl orthoacetates with an excess of TFAA afforded to trioxabicycles 4 in good yield. It is first example of fluorinated trioxabicyclo[3.3.1]nona-3,7-dienes.

Challenging chemical particularities of the *bis*-polyfluoroacylation of vinylic ethers will be presented.

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[2] S. Pazenok, N. Lui, I. Gerus, O. Balabon, WO2011073100 (2011); S. Pazenok, N. Lui, I. Gerus, WO2011073101 (2011)

## P1.8

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# A New Life for an Old Reagent: Fluoroalkyl Amino Reagents (FAR) as an Efficient Tool for the Synthesis of Diversely Fluorinated Pyrazoles

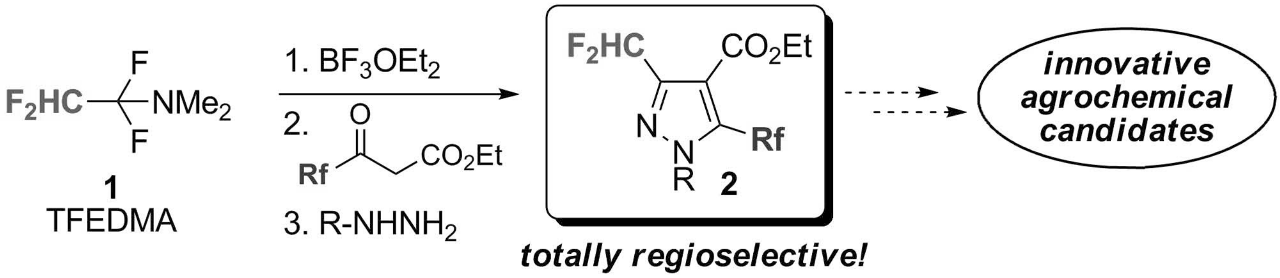
**F. GIORNAL [(a)], G. LANDELLE [(a)], S. PAZENOK [(b)], N. LUI [(b)], J. VORS [(c)], F. LEROUX [(a)]***

[(a)] Laboratoire de Chimie Moleculaire, UMR CNRS 7509, Universite de Strasbourg - STRASBOURG (FRANCE)
[(b)] Bayer Cropscience, Process Research - MONHEIM (GERMANY)
[(c)] Bayer Cropscience - LYON (FRANCE)

* frederic.leroux@unistra.fr

The introduction of fluorine atoms into lead structures is powerful strategy to optimize the properties of agricultural and pharmaceutical products. Hence, a significant rise in the number of active ingredients containing at least one fluorine atom has been observed over the last decades, and a recent survey estimated that as many as 18% of the pesticides on the market were fluorinated compounds.[1] Among the vast array of fluorine-containing functionalities fluoroalkyl pyrazoles have attracted considerable attention due to their potential enhanced biological properties.[2] In particular, a huge interest was accorded to the difluoromethyl pyrazole-carboxamides, which belong to the class of succinate-dehydrogenase inhibitors (SDHI) fungicides.

Despite recent advances in the synthesis of fluorinated pyrazoles, the preparation of pyrazoles bearing two fluorinated groups remains scarcely depicted in the literature, even if 3,5-bis(fluoroalkyl)-pyrazoles represent an important class of bioactive molecules. Herein we document the first practical method for the regioselective preparation of 3,5-bis(fluoroalkyl)-pyrazoles (2). Starting from commercially available fluoroacetoacetates and by using TFEDMA (1) as a convenient $CF_2H$-transfer reagent, this straightforward one-pot sequence affords highly substituted pyrazoles in good yields and excellent regioselectivity (>97:3, Scheme 1).[3] Furthermore, these carboxylate intermediates have been converted into the corresponding pyrazolic acids, valuable building blocks for the design of novel bioactive ingredients.



*Scheme 1. Regioselective one-pot preparation of 3,5-bis(fluoroalkyl)-pyrazoles.*

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[3] S. Pazenok, F. Giornal, G. Landelle, N. Lui, J.-P. Vors, F. R. Leroux, *submitted*.

## P1.9

# Difluoromethylbenzoxazole pyrimidine thioether (DFMB) derivatives as novel non-nucleoside HIV-1 reverse transcriptase inhibitors

**J. BOYER [(a)], A. MENOT [(a)], R. TERREUX [(b)], E. ARNOULT [(c)], J. UNGE [(d)], D. JOCHMANS [(e)], J. GUILLEMONT [(c)], M. MÉDEBIELLE [(a)]***

[(a)] Institut de Chimie et Biochimie Moléculaire et Supramoléculaire (ICBMS), UMR 5246, Equipe « Synthèse de Molécules d'Intérêt Thérapeutique (SMITH) » - VILLEURBANNE (FRANCE)
[(b)] Laboratoire BISI, UMR CNRS 5086 - LYON (FRANCE)
[(c)] Chemistry Lead Antimicrobial Research, Janssen-Cilag/Tibotec - VAL DE REUIL (FRANCE)
[(d)] MAX-Lab, Lund University - LUND (SWEDEN)
[(e)] Rega Institute for Medical Research - LEUVEN (BELGIUM)

* maurice.medebielle@univ-lyon1.fr

This presentation reports our past and current efforts towards the synthesis and antiviral properties of new difluoromethylbenzoxazole (DFMB) pyrimidine thioether derivatives as non-nucleoside HIV-1 reverse transcriptase inhibitors. By use of combination of structural biology study, docking and traditional medicinal chemistry, several members of this novel class were synthesized using single electron transfer chain process (radical nucleophilic substitution, $S_{RN}1$) and were found to be potent against wild-type HIV-1 reverse transcriptase, with low cytotoxicity but with moderate activity against resistant drug-resistant strains. One promising compound DFMB2 showed a significant $EC_{50}$ value close to 6.4 nM against wild-type IIIB, a moderate $EC_{50}$ value close to 54 µM against resistant double mutant (K1203N + Y181C) but an excellent selectivity index > 15477 ($CC_{50}$ > 100 µM) (Figure 1) [1].

Optimisation of these molecules toward activity on NNRTI-resistant HIV are now being pursued, with other modifications on the benzoxazole and pyrimidine rings based on our structural biology, current and new antiviral data and new molecular docking studies.

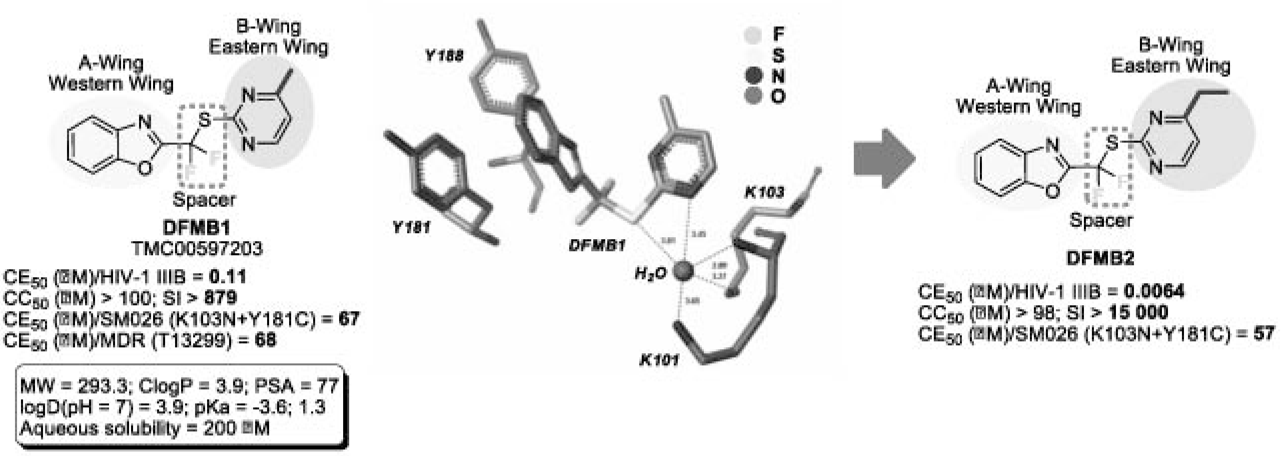

*Figure 1. Difluoromethylbenzoxazole (DFMB) pyrimidine thioethers as novel NNRTIs*

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[1] J. Boyer, E. Arnoult, M. Médebielle, J. Guillemont, J. Unge, D. Jochmans, *J. Med. Chem.*, **54. (2011)** 7974-7985.

## P1.10

# Trifluoromethyl-derived pyrido[3,2-d]pyrimidine derivatives from purines: synthesis and antimalarial activities

**B. OVADIA [a], R. STEYAERT [a], A. FAURIE [a], N. CHOPIN [a], T. GUERIN [a], S. PICOT [a], A. LAVOIGNAT [a], B. JOSEPH [a], M. MÉDEBIELLE [a]***

[a] Institut de Chimie et Biochimie Moléculaire et Supramoléculaire (ICBMS), UMR 5246, Equipe « Synthèse de Molécules d'Intérêt Thérapeutique (SMITH) » - VILLEURBANNE (FRANCE)

* maurice.medebielle@univ-lyon1.fr

Malaria causes 1.5 – 2.7 million deaths throughout the world. The widespread resistance of many *P. falciparum* strains to most readily available drugs, especially to Chloroquine (CQ), hinders malaria control and is therefore a major public health problem; there is an urgent need to find new chemotherapeutic agents with original mechanism of action. Over the last decade, inhibition of protein phosphorylation, performed by protein kinases (PKs), has emerged as a major opportunity for drug discovery development in numerous therapeutic areas. Among the PKs, cyclin-dependent kinases (CDKs) are essential for the regulation of eukaryotic cell cycle, and several enzymes of this family have been identified in *P. falciparum* (PfPk5, PfPk6, Pfmrk).

During the course of the syntheses of novel purine and bioisostere scaffolds as potential selective *P. falciparum* kinase inhibitors, we discovered a novel access to unknown pyrido[3,2-*d*]pyrimidines bearing a trifluoromethyl moiety (Figure 1), with some of them showing micromolar activity against *P. falciparum* clones of variable sensibility (CQ-sensitive 3D7 and CQ-resistant W2).

We will present the synthesis of a series of such derivatives starting from 2,6-dichloropurine, and their preliminary biological data evaluation as potent antimalarial agents.

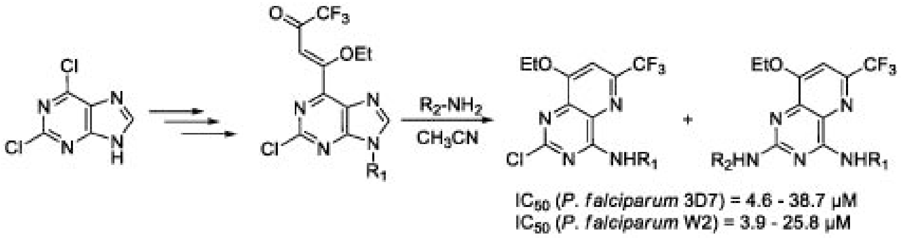


*Figure 1. New trifluoromethyl-derived pyrido[3,2-d]pyrimidines as potent antimalarial agents.*

## P1.11

# Some New Applications of Fluorine – Derived Reagents in Organic Chemistry

**J. GATENYO** [(a)]*, **I. VINTS** [(a)], **S. ROZEN** [(a)]

[(a)] TEL AVIV UNIVERSITY, CHEMISTRY - TEL AVIV (ISRAEL)

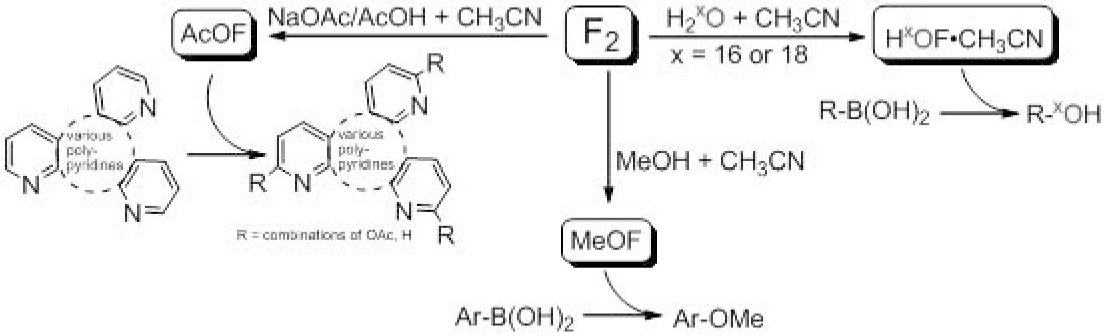
* julialur@post.tau.ac.il

Years ago the exploration of the synthetic potential of $F_2$ has been undertaken in our department. Almost immediately it was clear that elemental fluorine (1 – 20% diluted with nitrogen) has enormous synthetic potential. Not only that it could perform regio- and stereospecific electrophilic fluorinations, but it could also be used for preparation of novel reagents, which are able to construct fluorine-free organic compounds, that are either very difficult or even impossible to otherwise make. Some of these reagents are:

- The $HOF \times CH_3CN$ complex, easily prepared by bubbling dilute fluorine through aqueous acetonitrile. It is considered to be one of the best oxygen transfer agents in chemistry today. Employing $^{18}O$-labeled water results in heavy oxygen labeled reagent ($H^{18}OF \times CH_3CN$). This allowed us to prepare any oxygen-18 labeled alcohol at will.

- Acetyl hypofluorite ($CH_3COOF$) is also easily made from sodium acetate and $F_2$. It proved to be a very useful reagent for fluorination of activated aromatic compounds, for activation of a CH bond in polypyridine systems, for constructing a-fluoro carbonyl derivatives and for use in Positron Emitting Tomography (PET).

- Fluorine can react with methanol in acetonitrile to produce MeOF. It is unique in a sense that it is the only source for the novel electrophilic methoxylium moiety "MeO+" and as a such has a potential to preform unique reactions. This molecule reacts with activated aromatic boronic acids to produce oxygenated aromatic derivatives. Also, MeOF is an excellent tool for introducing the short-live positron emitting $^{11}C$ into compounds important for positron emitting tomography.



## P1.12

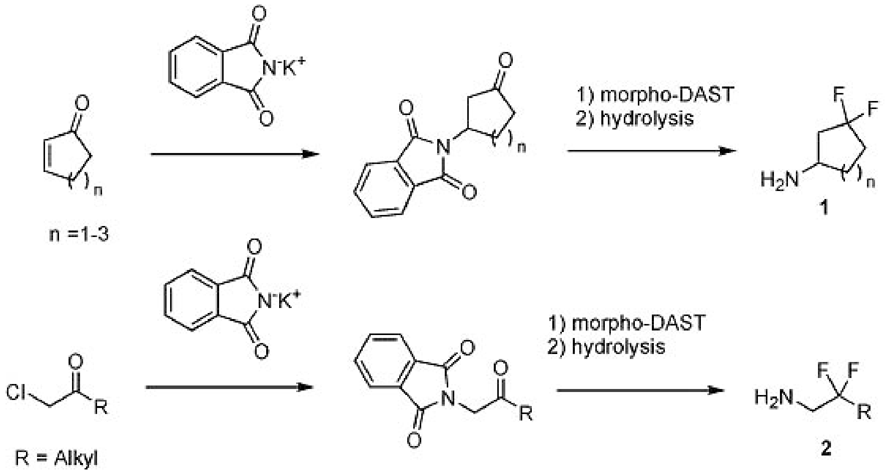
# Synthetic Approach to New Difluoromethelene Containing Amines

**G. POSTERNAK [(a)], I. KONDRATOV [(b)]*, N. TOLMACHEVA [(a)], A. TOLMACHEV [(a)], K. TARASENKO [(b)], O. HILCHEVSKY [(b)]**

[(a)] ENAMINE LTD, CHEMISTRY - KYIV (UKRAINE)
[(b)] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)

* Vanya_ko@mail.ru

Introduction of Fluorine into definite positions of biologically active compounds is a convenient strategy to improve both potency and ADME-parameters of the substance [1]. This approach is widely used in the modern medicinal chemistry. It is difficult to find an example in medicinal chemistry practice where Fluorine or Fluorine containing substitutions were not used during the hit-to-lead optimisation.



Since the most of medicinal chemistry project deal with application of building-blocks it is important for medicinal chemist to have an available and diverse set of Fluorine containing building blocks such as Fluorine containing aliphatic amines. At the same time many simple combinations of fluorine with carbon and nitrogen atoms are still unknown. Therefore we started developing the synthetic method towards different hitherto unknown fluorinated aliphatic amines.

During the study it was found an effective approach to γ,γ-difluoro containing cyclic amines 1 starting from the corresponding α,β-unsaturated cyclic ketones. On the other hand the corresponding β,β-difluoroamines 2 were obtained starting from acyclic α-chloroketones. In both cases Potassium phthalimide was used to introduce the protected amino group into the molecule. Some other examples of the obtained fluorinated amines as well as the synthetic pathways and particularities of the chemistry will be presented in detail.

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[1] W. K. Hagmann *J. Med. Chem.* 51 (**2008**) 4359-4369.

## P1.13

# Synthesis and Evaluation of Fluorinated Analogues of S1P Antagonists

**V. PUSHPA PRASAD [a]*, P. KEUL [b], L. BODO [b], M. SCHÄFERS [b], G. HAUFE [a]**

[a] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)
[b] European Institute for Molecular Imaging, Universität Münster - MÜNSTER (GERMANY)

* prasadvysakh1986@gmail.com

Sphingosine-1-phosphate (S1P) [1,2] is a bioactive lysophospholipid mediator that is mainly released from activated platelets. A wide variety of biological cellular responses to S1P have been ascribed to the presence of five S1P subtype receptors (S1P1 to S1P5), that belong to the family of G protein-coupled receptors. Among the five known high-affinity receptors, the S1P1 receptor is expressed by many cell types, including endothelial and cardiac cells. Although the receptor activation has been studied using various agonists, there are not many suitable antagonists available. At present there are no tools available to visualise the S1P/S1P1 receptor in vivo.

A couple of years ago, Sanna et al. [3] reported a S1P1 inhibitor molecule (R)-3-amino-4-(3-hexylphenyl-amino)-4-oxobutylphosphonic acid (W 146, Fig. 1), which has been used in in vivo experiments to provide insights into the role of S1P/S1P1 signalling.

We have synthesized several fluorinated analogues of W146 (Fig. 2) and tested their activities as antagonists for S1P receptors. Introduction of a fluorine atom to the alkyl chain of W 146 is expected to modify the lipophilicity and hydrophilicity, which might lead to S1P antagonists with different selectivity. The fluorine in terminal position in turn opens up the possibility to develop these molecules as radio tracers to visualize S1P receptors using PET in vivo.

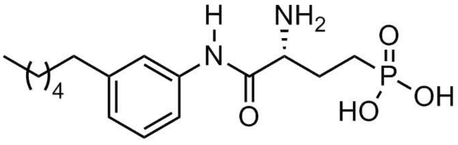

Fig. 1. W 146

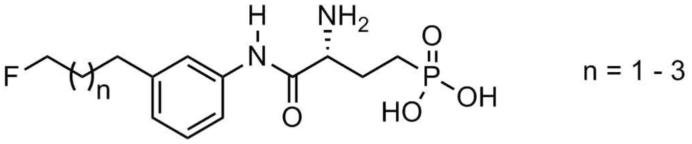

Fig. 2. Fluorinted derivatives of W 146

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[1] H. Rosen, E. J. Goetzl, *Nat. Rev. Immunol.*, **5** (2005) 560-570.

[2] H. Rosen, P. J. Gonzalez-Cabrera, M. G. Sanna, S. Brown, *Ann. Rev. Biochem.*, **78** (2009) 743-768.

[3] M. G. Sanna, S.-K. Wang, P. J. Gonzalez-Cabrera, A. Don, D. Masolais, M. P. Matheu, S. H. Wei, I. Parker, E. J. Jo, W.-C. Cheng, M. D. Kahalan, W.-H. Wong, H. Rosen, *Nature Chem. Biol.*, **2** (2006) 434-441.

## P1.14

# Synthesis of Trifluoromethylated Pyrroles

**T. BILLARD [a]*, O. MARREC [a], B. LANGLOIS [a], J. VORS [b], S. PAZENOK [c]**

[a] UNIVERSITÉ CLAUDE BERNARD - LYON 1, ICBMS (UMR CNRS 5246) - LABORATOIRE SURCOOF - VILLEURBANNE (FRANCE)
[b] Bayer Cropscience - LYON (FRANCE)
[c] Bayer Cropscience, Process Research - MONHEIM (GERMANY)

* thierry.billard@univ-lyon1.fr

Among heterocycles, the pyrroles constitute the core of a large number of alkaloids and many other physiologically active compounds, which make them strongly attractive as synthetic targets for further investigation.

Furthermore, the influence of fluorinated moiety onto organic molecules is now well-known to modulate properties of compounds. In particular, the trifluoromethyl group is of great interest in a large panel of applications.

Consequently, new methods to easily synthesize functionnalized trifluoromethylated pyrroles are of great interest.

We recently described an easy synthesis of β-trifluorometylated $\Delta^1$-pyrrolines starting from β-trifluoromethylated enones. Such products can be easily oxidized to provide an valuable access to variously substituted pyrroles.

## P1.15

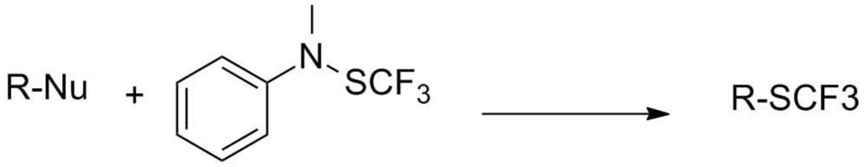
# Electrophilic Trifluoromethanesulfenylation of nucleophilic Species with Trifluoromethanesulfenamides

**S. ALAZET** [(a)]*, **F. BAERT** [(a)], **J. COLOMB** [(a)], **T. BILLARD** [(a)]

[(a)] UNIVERSITÉ CLAUDE BERNARD - LYON 1, ICBMS (UMR CNRS 5246) - LABORATOIRE
SURCOOF - VILLEURBANNE (FRANCE)

* sebastien.alazet@gmail.com

More and more applications for fluorinated molecules are being found in various fields, in particular in the fields of medicinal chemistry and agrochemistry. In recent years, there has been growing interest in the association of the trifluoromethyl group with heteroatoms such as $CF_3O$ or $CF_3S$. The $CF_3S$ moiety is of particular interest, because of its high hydrophobicity parameter ($\pi_R$=1.44). Consequently, compounds bearing this group are potentially important targets for applications in pharmaceuticals and agrochemicals. A more elegant approach is the direct trifluoromethanesulfenylation of substrates. We have, recently, described an easy synthesis of a family of reagents that are stable and easy to handle, namely the trifluoromethanesulfenamides. These reagents have already demonstrated their potential in the electrophilic trifluoromethanesulfenylations. These results contribute to validate these reagents as a valuable alternative to $CF_3SCl$ for trifluoromethanesulfenylation reactions.



Nu = Grignard or organolithium reagents
Deprotoned allynes
Activated alkenes

## P1.16

# Synthesis of fluorinated exo-glycals as a potent glycosidases inhibitor via modified Julia reaction

**S. HABIB [(a)], F. LARNAUD [(b)], E. PFUND [(b)], T. LEQUEUX [(b)]*, C. ORTIZ MELLET [(c)], T. MENA [(c)], P.G. GOEKJIAN [(a)], D. GUEYRARD [(a)]**

[(a)] Université de Lyon, ICBMS, LCO2 - VILLEURBANNE (FRANCE)
[(b)] LCMT - University of Caen - CAEN (FRANCE)
[(c)] University of Sevilla - SEVILLA (SPAIN)

* thierry.lequeux@ensicaen.fr

Selective incorporation of fluorine atom(s) into organic compounds can often impart many beneficial properties, which has stimulated the development of highly efficient and practically useful synthetic methods for the preparation of fluorinated organic compounds.[1]

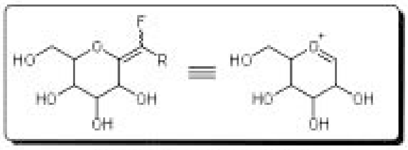
One of the limitations in the use of *O*-glycosides for drug development remains the low metabolic stability of the anomeric bond which limits the bioavailability of carbohydrates-based drugs.

In this context we report a concise and efficient method to synthesize tri and tetra-substituted fluorinated *exo*-glycals.[2] The degree of substitution of the lactones, the choice of protecting groups, and the structure of the functionalized fluorinated sulfones were evaluated in order to determine the scope and limitations of this reaction.

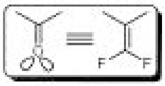
We used our method to synthesize a range of compounds which was evaluated as glycosidase inhibitor. These molecules are analogs of the transition state due to their conformation.[3]

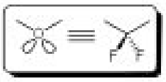
In addition, fluoralkanes and fluoroalkenes are isopolar and isosteric analogues of various functional groups, such as ketones or ethers.[4] For these reasons, we hope that fluorine atom can mimic *O*-glycoside during the enzymatic process.

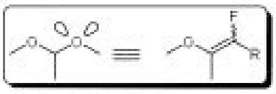
**Synthesis of tri and tetra-substituted fluorinated *exo*-glycals**



**Glycosidase Inhibitor**







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## P1.17

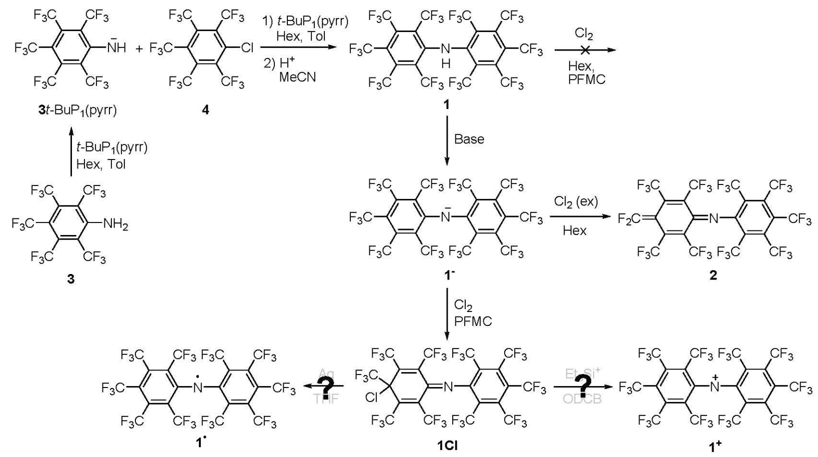
# Bis[pentakis(trifluoromethyl)phenyl]amine and its derivatives

**A. KÜTT** [(a)]*, **I.A. KOPPEL** [(a)]

[(a)] UNIVERSITY OF TARTU, INSTITUTE OF CHEMISTRY - TARTU (ESTONIA)

* agnes.kutt@ut.ee

Bis[pentakis(trifluoromethyl)phenyl]amine 1, especially its anion $1^-$ is used to prepare starting material for the target substances - aminyl radical and nitrenium cation. Aminyl radicals as well as nitrenium cations are very reactive intermediates and often exists only for very short time in the solution. Hereby, some methods for trying to isolate those substances are presented.



## P1.18

# $CF_3$ labelled substrate of 20S proteasome to measure $IC_{50}$ of proteasome inhibitors by $^{19}$F NMR spectroscopy

**S. ONGERI** [(a)]*, **M. KEITA** [(a)], **J. KAFFY** [(a)], **E. MORVAN** [(a)], **C. TROUFFLARD** [(a)], **B. CROUSSE** [(b)]

[(a)] UNIVERSITÉ PARIS SUD, MOLÉCULES FLUORÉES ET CHIMIE MÉDICINALE, UMR CNRS 8076, LABEX LERMIT - CHÂTENAY-MALABRY (FRANCE)

[(b)] Faculté de Pharmacie Université Paris Sud, BIOCIS MOLECULES FLUORÉES ET CHIMIE MÉDICINALE - CHÂTENAY-MALABRY (FRANCE)

* sandrine.ongeri@u-psud.fr

Regulator of a vast array of vital cellular processes including cell-cycle progression, apoptosis and antigen presentation, the proteasome represents a major therapeutic target. Therefore, selective inhibitors of the proteasome are promising candidates to develop new treatments for diseases like inflammation, immune diseases and cancer. Bortezomib, the first proteasome inhibitor approved by the FDA to treat multiple myeloma, and many described proteasome inhibitors interact covalently with the active site of the enzyme through an electrophilic reactive function. Non-covalent inhibitors have been less widely investigated [1]. Devoid of reactive function prone to nucleophilic attack, they could offer the advantage of an improved selectivity and bioavailabilty, a less excessive reactivity and instability often associated with side effects in therapeutics. While fluorinated bioactive compounds have been attracting considerable attention, the introduction of fluorine in proteasome inhibitors have been very scarcely reported [1]. We reported the first synthesis of $CF_3$-β-hydrazino acid and the first representatives of a new class of non-covalent 20S inhibitors based on a central fluorinated b-hydrazino acid scaffold [2]. We describe here a- and β-hydrazino acid-based pseudopeptides that inhibit the chymotrypsin-like (CT-L) activity of eukaryotic 20S proteasome [3].

A powerful role for fluorine is as a tag for $^{19}$F NMR, because unlike the $^{1}$H and $^{13}$C nuclei, there is no background signal for $^{19}$F [4]. We present here the development of an original fluorinated substrate of the CT-L proteasome active site. We labelled the substrate with a $CF_3$ moiety and utilized $^{19}$F NMR spectroscopy for the detection of the starting and enzymatically modified substrates. The method allowed us to measure reliable $IC_{50}$ values of our synthesized compounds [3]. This novel method could be exploited for the screening of large compounds collection.

Figure 1

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## P1.19

# Application of Skraup Reaction for Synthesis of Novel Fluorinated Phenanthrolines

**C. LÜDTKE** [(a)] , **A. HAUPT** [(a)], **N. KULAK** [(a)]*

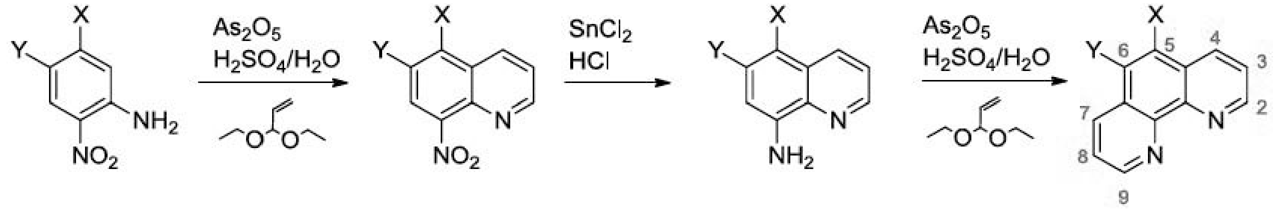
[(a)] FREIE UNIVERSITAT BERLIN, INORGANIC CHEMISTRY - BERLIN (GERMANY)

* nora.kulak@fu-berlin.de

Heterocyclic compounds show many different biological activities and therefore are of great interest for medicinal applications. One of these compounds is 1,10-phenanthroline (phen), whose copper complexes $[CuL_x]^{2+}$ (L = phen, x = 1, 2) are able to cleave DNA in an oxidative pathway [1]. Substituents like electron-withdrawing groups in position 5 of phen can increase these cleavage activity [2].

Our aim was to synthesize phen derivatives including fluorine atoms and fluorine-containing groups in position 5 or 5 and 6. The Skraup reaction appeared to be a useful synthesis strategy for the generation of these derivatives.

This study was based on experiments by Lee *et al.* to form 5-fluoro-8-amino quinoline [3]. Although the Skraup reaction is described to be unsucessful for the generation of 5-(trifluoromethyl)phen [4], we were able to synthesize different known and unknown fluorine-containing phenanthroline derivatives including 5-(trifluoromethyl)phen in acceptable yields and excellent purities in a straightforward strategy. The starting material is always a fluorine containing nitro aniline-derivative and the method can be applied to different phen analogues.



*Synthesis of 5-fluorophen (X = F, Y = H), 5,6-difluorophen (X = F, Y = F) and 5-(trifluoromethyl)phen (X = H, Y = CF3)*

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## P1.20

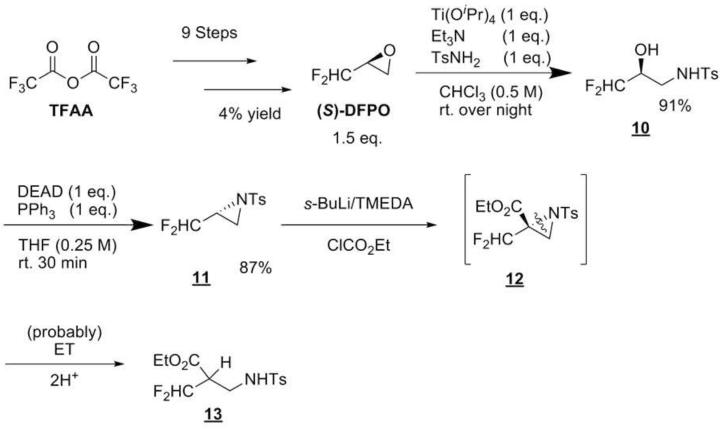
# Synthesis of optically pure 2-difluoromethyl aziridine.

**S. HIRAMATSU** [(a)]*

[(a)] OKAYAMA UNIVERSITY, HETERO ATOM CHEMISTRY - OKAYAMA (JAPAN)

* en20246@s.okayama-u.ac.jp

In our previous report, we described on systematic preparation of α-trifluoromethylamino acids from 2,3-epoxy-1,1,1-trifluoropropane (TFPO) via stereospecific reactions [1]. α-Difluoromethylamino acids are also important class of compounds. Here we planned a systematic preparation of optically pure difluoromethyl amino acids from 2,3-epoxy-1,1-difluoropropane (DFPO). (*S*)-DFPO was synthesized from trifluoroacetic anhydride (TFAA) in 4% yield. 2-Difluoromethyl aziridine was synthesized from (*S*)-DFPO in 52% yield via 2 steps. Compound 11 did not react with $^n$BuLi with ClCO$_2$Et. As a result of the examinations, deprotonation of compound 11 was achieved by *sec*-BuLi/TMEDA [2]. However, the product was compound 13, a over reduction product. We would like to make a presentation on our further result of examinations and synthesis of α-difluoromethylamino acids.



*Scheme 1.*

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[2] a) Satoh, T. *Chem. Rev.* **96,** (1996), 3303-3325. b) Hodgson, D. M.; Gras, E. *Angew. Chem. Int. Ed*. **41**, (2002), 2376-2378.

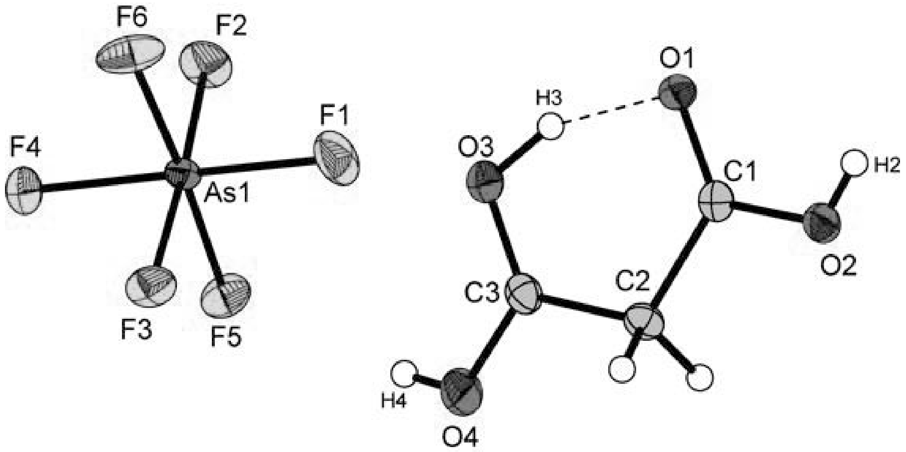
# P1.21

## Protonation of malonic acid: preparation and characterization of the mono- and diprotonated malonic acid

**M. SCHICKINGER** [(a)]*, **K. LUX** [(a)], **A. KORNATH** [(a)]

[(a)] LUDWIG-MAXIMILIAN UNIVERSITY, DEPT. OF CHEMISTRY - MUNICH (GERMANY)

* Manuel.Schickinger@cup.uni-muenchen.de



Malonic acid was protonated in the systems HF/$SbF_5$ and HF/$AsF_5$, respectively. Beside the expected monoptotonation to the $[(OH)_2CCH_2COOH]^+$ cation, also the diportonated species $[(HO)_2CCH_2C(OH)_2]^{2+}$ was observed. The products have been characterized by vibrational spectroscopy and single-crystal x-ray analyses. The experimental results are discussed together with quantum chemical calculations.

## P1.22

# Synthesis of fluorinated α-galactosylceramide

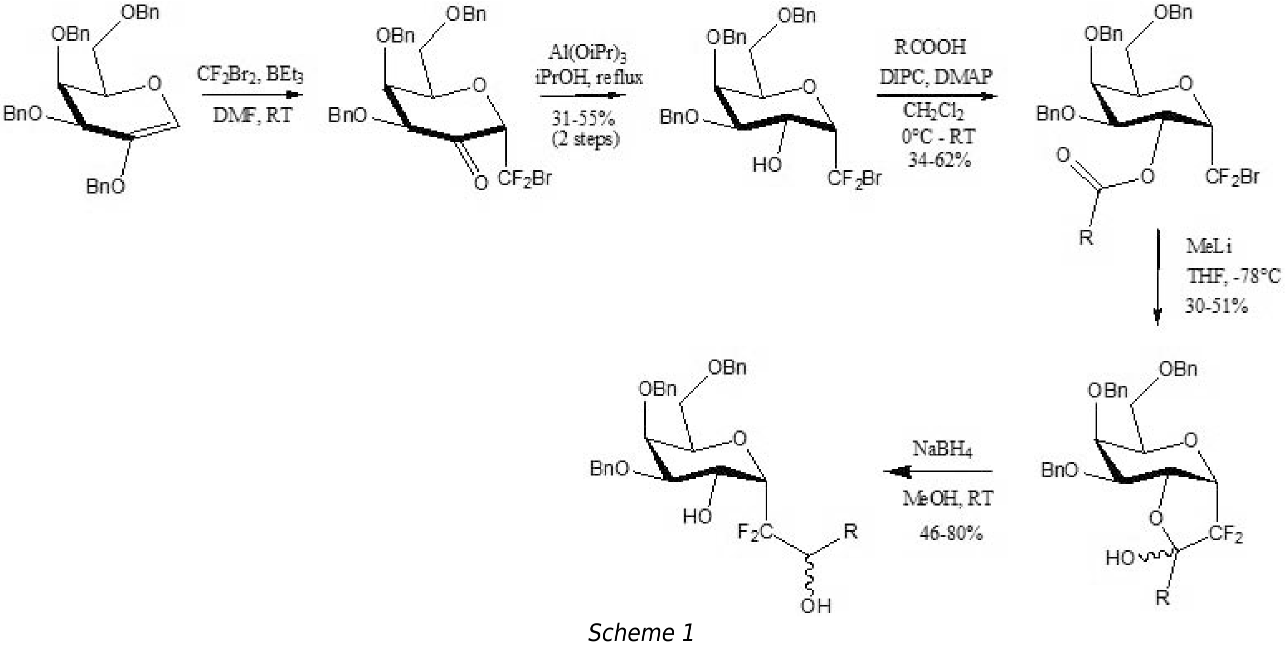
**N. VAN HIJFTE [(a)]*, S. COLOMBEL [(a)], T. POISSON [(a)], E. LECLERC [(b)], X. PANNECOUCKE [(a)]**

[(a)] IRCOF - INSA de Rouen, UMR 6014 COBRA - MONT SAINT-AIGNAN (FRANCE)
[(b)] Institut Charles Gerhardt - MONTPELLIER (FRANCE)

* nathalie.van-hijfte@insa-rouen.fr

Glycoconjugates are known to play a crucial role in many biological events, such as protein structure modulation or cell-cell recognition, and thus became highly attractive targets for drug research.[1] However, as with many carbohydrate-based drugs, glycopeptides might often suffer from a low metabolic stability due to the cleavage of the anomeric bond. It thus appeared interesting to develop non-hydrolyzable candidates such as fluorine glycomimetics.[2]

A novel methodology for the synthesis of $\alpha$-$CF_2$-glycosides is described, based on the radical addition of $CF_2Br_2$ to glycals, followed by a Meerwein-Ponndorf-Verley reduction.[3] A one-pot Br/Li exchange/nucleophilic addition sequences provides an interesting route for a synthesis of fluorinated $\alpha$ -galactosylceramide analogues (Scheme 1).[4] This methodology was applied to the synthesis of fluorinated KRN7000 analogues.



*Scheme 1*

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[1] H.-J. Gabius, H.-C. Siebert, S. André, J. Jiménez-Barbero, H. Rüdiger, *Chem. Bio. Chem.*, **5** (2004) 740.
[2] (a) K. W. Pankiewicz, *Carbohydrates Res.*, **327** (2000) 87. (b) T. F. Herpin, W. B. Motherwell, J.-M. Weibel, *Chem. Commun.*, (1997) 923.
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## P1.23

# Fluoroalkylation of 5,10,15-Tris(pentafluorophenyl)corrole

**R. DU** [(a)]*, **Q. CHEN** [(a)], **J. XIAO** [(a)]

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)

* duruobing@sioc.ac.cn

The porphyrin-type compounds have widely used as catalysts, chemical sensors and photosensitizers. Because of the above-mentioned potential use in these scientific areas, we developed several methods for synthesizing fluoroalkated corroles.[1]

On the basis of our investigations on fluoroalkylation of porphyrins,[2]we tried to expand the sulfinatodehalogenation reaction to corroles. Treatment of 1 with $ClC_4F_8I$ and $Na_2S_2O_4$ in DMSO at room temperature led to monofluoroalkylated corroles 2a and 2b in 1:1(Figure 1). The amounts of reactants $R_FI$ and $Na_2S_2O_4$ used as well as reaction temperatures had a great influence on the yield of 2. Increasing the amounts of $ClC_4F_8I$ and $Na_2S_2O_4$ could not provide multifluoroalkylated corroles and serious degradation of corroles was observed. It should be mentioned that the DMSO solution of $ClC_4F_8I$ should be added dropwise over a period of two hours in order to obtain monofluoroalkylated corrole.Elevated reaction temperatures induced the formation of many side products and made the separation more difficult. Usually, $NaHCO_3$ was added to control the mild decomposition of $Na_2S_2O_4$ as in the case of sulfinatodehalogenation of perfluoroalkyliodides for porphyrins. However, using $NaHCO_3$ as a base under similar conditions in this reaction dramatically reduced the yield of fluoroalkylated corroles, which might result from the serious decomposition of the products aroused by the base.

Under the similar conditions a,w-diiodoperfluoroalkane $I(CF_2)_nI$ (n = 3 or 4) could be successfully applied to the reaction of corroles, yielding the expected intramolecularly radical cyclized products (Figure 1).

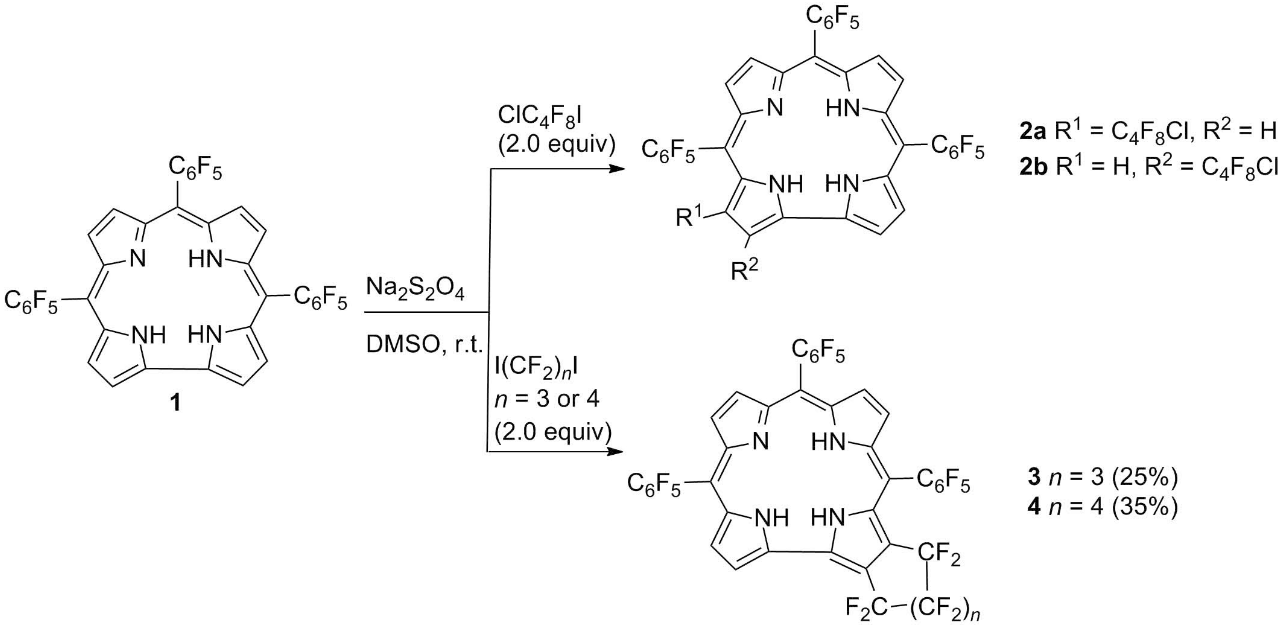

*Figure 1: Fluoroalkylation of corrole*

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## P1.24

# Fluorinated building blocks for Hyaluronic Acid subunits synthesis

**K. KORONIAK-SZEJN [a]*, M. BARDZINSKI [a], J. JUREK [a]**

[a] Adam Mickiewicz University, FACULTY OF CHEMISTRY - POZNAN (POLAND)

* katarzyna.koroniak@amu.edu.pl

Synthetically available carbohydrates are of great interest for the development of carbohydrate-based drugs as well as new drug delivery systems. One of the polysaccharides of great interest is the hyaluronic acid (HA). Due to its exceptional characteristics, such as water-binding, visco-elastic and biological properties HA not only adds new and improved attributes to existing formulations but also offers many benefits in the drug delivery area.

The main goal of this work was the design and synthesis of hydrophilic HA-units functionalized with different hydrophobic moieties (mainly fluorinated) in order to enhance lipophilicity of the polar HA. It is noteworthy that finding the right amphiphilicity of the novel drug delivery carriers is a crucial step in allowing this delivery platform to pass the cellular membrane and reach the targeted cells.

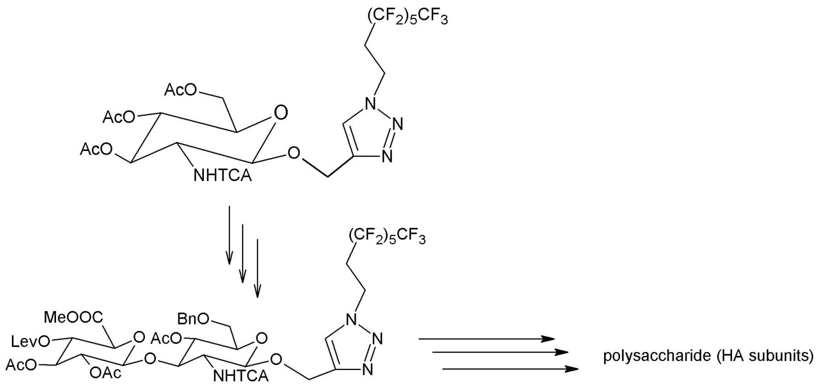

Fig. 1 Synthesis of modified HA-subunits

It is also known that such molecules, composed of biocompatible and amphiphilic conjugates could exhibit prolongated circulation in blood and preferential accumulation at tumor tissues [1,2] therefore allowing for very desired in modern drug delivery approaches targeted and sustained release. In this paper we present the preparation of the building blocks for HA-subunits synthesis derivatized, *via*"c*lick reaction*", with the fluorinated alkyl chains (Fig. 1).

Project funded by the grant from Foundation for Polish Science within the *HOMING Plus* program.

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[2] A. J. Day and G. D Prestwich *J. Biol. Chem.* ***277*** (2002), 4585 – 4588.

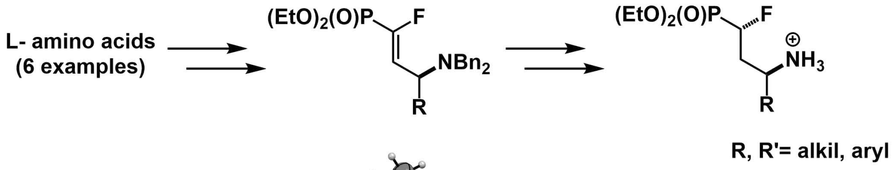
## P1.25

# Preparation and characterisation of novel *α*-fluorinated-*γ*-aminophosphonate oxalates

**M. KAZMIERCZAK** [(a)]*, **G. DUTKIEWICZ** [(a)], **M. KUBICKI** [(a)], **H. KORONIAK** [(b)]

[(a)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY - POZNAN (POLAND)
[(b)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* marcin.kazmierczak@amu.edu.pl



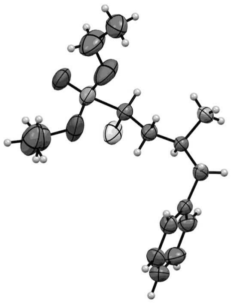


*Fig. 1.*

Organophosphorus compounds are important substrates in biochemical processes. They are potent bioactive molecules used as agrochemicals and pharmaceuticals, as well as effective enzyme inhibitors [1]. It is also known, that the introduction of fluorine atom(s) into organic molecules may change their chemical, physical and biological properties [2]. These fundamental observations are the conceptual base for studies on new organophosphorus–fluorine containing compounds. For example, it has been shown that fluorinated aminophosphonates are useful inhibitors of many enzymes, their cytotoxic and antibacterial activity has been reported [3].

Our synthetic strategy towards novel *α*-fluoro-*γ*-aminophosphonate oxalates, their crystal structures as well as applications in medicinal chemistry will be presented.

Acknowledgments: The research was supported by Wroclaw Research Centre EIT+. BioMed (POIG.01.01.02-02-003/08)

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[3] Romanenko, V. D.; Kukhar, V. P. *Chem. Rev.*, **106** (2006) 3868-3935.

## P1.26

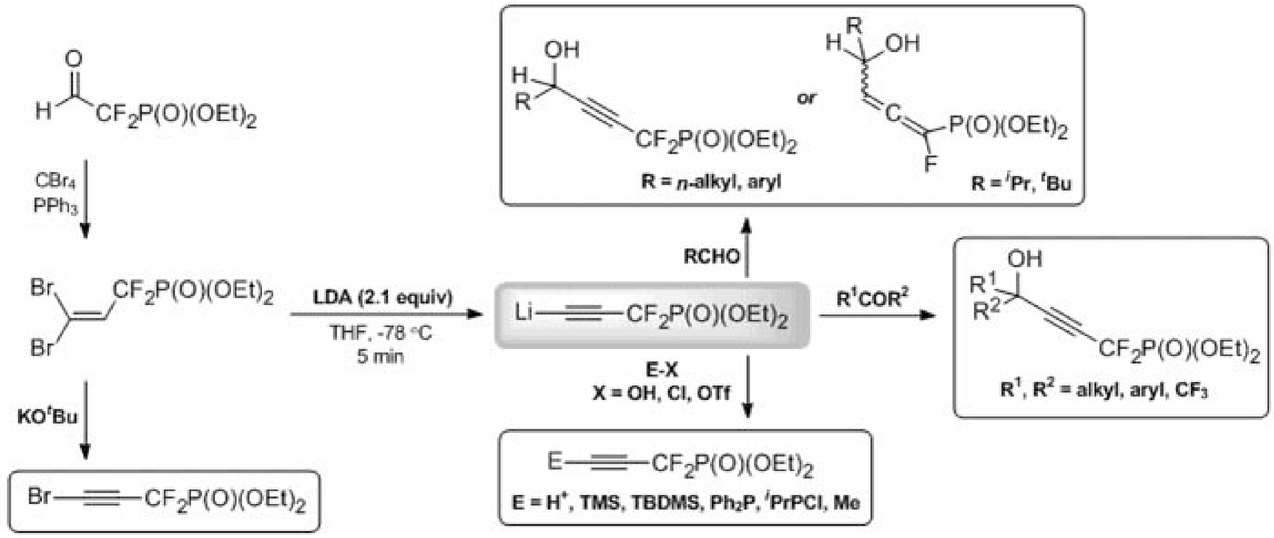
# Synthesis of (α,α-Difluoropropargyl)phosphonates via Aldehyde-to-Alkyne Homologation

**R. PAJKERT [a]*, G. ROESCHENTHALER [a]**

[a] JACOBS UNIVERSITY BREMEN GGMBH, SCHOOL OF ENGINEERING AND SCIENCE - BREMEN (GERMANY)

* r.pajkert@jacobs-university.de

An efficient synthetic methodology to a series of novel alkynes bearing difluoromethylenephosphonate function *via* Corey-Fuchs-type sequence starting from (diethoxyphosphoryl)difluoroacetic aldehyde is described. Dehydrobromination of the intermediate (3,3-dibromodifluoroallyl)phosphonate with potassium *tert*-butoxide gave rise to the corresponding bromoalkyne, whereas upon treatment with lithium base, the generation of (diethoxyphosphoryl)difluoropropynyl lithium has been achieved for the first time. The synthetic potential of this lithium reagent was further demonstrated by its reactions with selected electrophiles such as aldehydes, ketones, triflates, chlorophosphines or chlorosilanes leading to the corresponding propargyl phosphonates in good-to-excellent yields. However, in the case, of sterically hindered aldehydes, (α-fluroallenyl)phosphonates were the solely isolated products.



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[1] R. Pajkert, G.-V. Röschenthaler, *J. Org. Chem.*, (2013) accepted

## P1.27

# Construction of selected heterocycles with per- and polyfluoroalkoxy groups based on aliphatic precursors

**Y. DAVYDOVA [a], T. SOKOLENKO [b]*, Y. YAGUPOLSKII [a]**

[a] Institute of Organic Chemistry, National Academy of Sciences of Ukraine - KYIV (UKRAINE)
[b] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, DEPARTMENT OF ORGANOFLUORINE COMPOUNDS - KYIV (UKRAINE)

* taras_sk@ukr.net

Polyfluoroalkoxy groups hold a considerable promise for the fine-tuning of technical and biological properties of organic molecules. While aromatic α-fluorinated ethers since the first publication in 1955 by L.M. Yagupolskii were extensively studied and widely used as pharmaceuticals and crop protection agents, heterocyclic compounds with such a group directly attached to a heterocyclic ring are rare. Some pyrazole, pyridine and pyrimidine derivatives were obtained by direct polyfluoroalkylation of their hydroxy derivatives with difluorocarbene or fluoroolefines. This approach cannot be applied for wide range of heterocycles due to the dominance of the keto-form over the hydroxy one in their structures.

In our opinion, the synthesis of the heterocyclic rings from aliphatic per- and polyfluoroalkoxy containing precursors is an attractive offer. Thus we focused our attention on this problem solution.

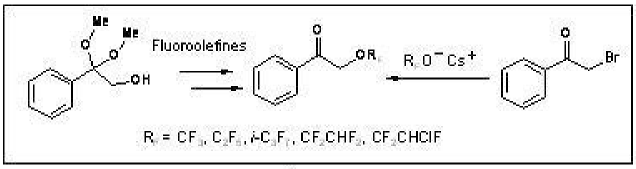

Fig. 1.

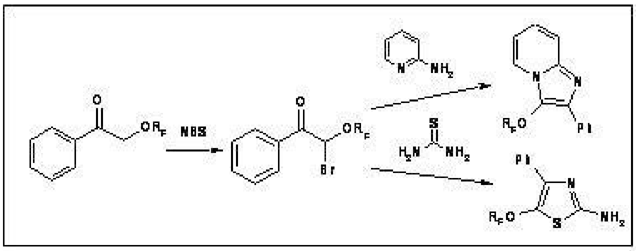

Fig. 2.

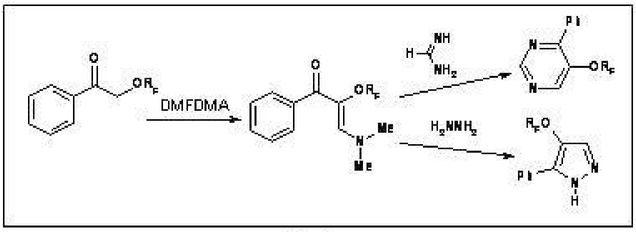

Fig. 3.

Acetophenones with poly- and perfluoroalkoxygroups can be conveniently prepared via the addition of 2,2-dimethoxy-2-phenylethanol to fluoroolefins at the atmospheric pressure or by the action of cesium perfluoroalcoholates on α-bromoacetophenones (Fig. 1).

α-Bromo-α-fluoroalkoxyacetophenones, available from corresponding acetophenones, are convenient precursors for various imidazole or thiazole derivatives preparation (Fig. 2).

We found out that α-fluoroalkoxyacetophenones readily react with dimethylformamide dimethylacetal (DMFDMA) leading to enaminones with fluoroalkoxy groups. Such compounds are convenient precursors for various pyrimidine or pyrazole derivatives syntheses (Fig. 3).

## P1.28

# Synthesis of Trifluoromethylated γ-Aminophosphonates by Nucleophilic Aziridine Ring Opening

**T. CYTLAK [(a)]*, M. SAWELIEW [(a)], G. DUTKIEWICZ [(a)], M. KUBICKI [(b)], H. KORONIAK [(b)]**

[(a)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY - POZNAN (POLAND)
[(b)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* cytlak@amu.edu.pl

Aziridine derivatives are valuable functionalized building blocks for the asymmetric synthesis of amino phosphonates because of their ability to undergo highly regio- and stereospecific ring-opening reactions. [1]

Amino phosphonates are an important class of compounds because of their unique utilities as antibiotics, herbicides, antifungal, enzyme inhibitors, and pharmacological agents. Among the various types of aminophosphonates, the γ-aminophosphonates (originally were isolated from microorganisms) can play significant role in medicine (e.g. matrix metaloproteinases inhibitors, anti-infalammatory drugs). Their derivatives can also act as analogues of γ-amino acids, and as such they constitute important motifs in medicinal chemistry. [2]

Futhermore, the presence of $CF_3$ group in aziridine ring constitutes a promising route to fluorinated amino acids analogues. The introduction of fluorine atoms in organic molecules often results in a deep modification of physical, chemical and biological properties of the parent compounds. [3]

In this communication, we would present our synthetic strategy towards novel trifluoromethylated γ-aminophosphonates (Fig. 1).

Their absolute configuration was confirmed by X-ray analysis. The crystal structure of diethyl (1R,2R,3S)-3-(benzylamino)-4,4,4-trifluoro-2-(4-fluorophenylthio)-1-hydroxybutylphosphonate, as an example, is presented in Fig. 2.

Acknowledgments: „The research was supported by Wroclaw Research Centre EIT+. BioMed (POIG.01.01.02-02-003/08)’’

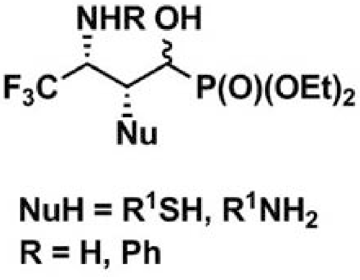

Fig. 1

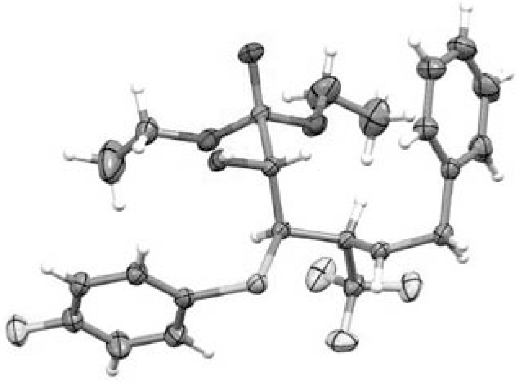

Fig. 2

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## P1.29

# Synthesis of Fluorinated Structural Analogues of FTY 720 (Gilenya®) and Sphingosine-1-phosphate

**R. SHAIKH [a]*, S. SCHILSON [a], P. KEUL [b], L. BODO [b], M. SCHÄFERS [b], G. HAUFE [a]**

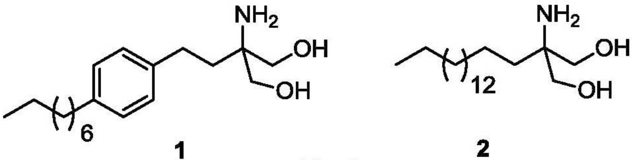
[a] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)
[b] European Institute for Molecular Imaging, Universität Münster - MÜNSTER (GERMANY)

* rizwansh.org12@gmail.com

The intracellular and extracellular effect of sphingosine-1-phosphate (S1P) is mediated by its interaction with G-protein coupled receptors (GPCRs) further subdivide into $S1P_{1-5}$ receptors [1]. Analysis of S1P receptor subtypes in mice indicated that the heart and lung have the highest expression of $S1P_1$, $S1P_2$ and $S1P_3$. Expression of $S1P_4$ deals with lymphoid and haematopoietic tissues and $S1P_5$ with midbrain and hindbrain [2].

In adddition to the discovery of FTY 720 (Gilenya®) 1 as a potent agent against autoimmune diseases and its approval for treatment of Multiple Sclerosis in 2011, several other $S1P_1$ subtype specific agonists and structural analogues of S1P such as 2 have been discovered showing promising binding affinity with GPCRs [3]. These discoveries lead to world-wide interest in subtype selective binding of S1P ligands with S1PRs to study expressions of GPCRs.

We have synthesised fluorinated structural analogues of 1 and 2 and observed that ω-fluorinated derivatives are biologically most active making them promising candidates for $S1P_1$ receptor agonists [4].



**1** **2**

Fig. 1.

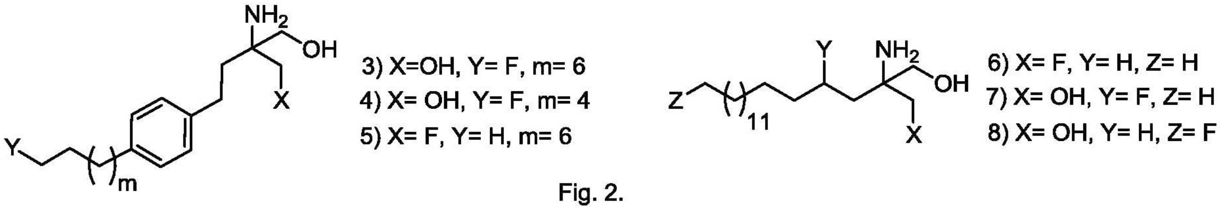


Fig. 2.

*Figure 1. FTY 720 (1), and Analogue (2), Figure 2. Compounds synthesised and studied within this project*

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## P1.30

# The 1,3-Dipolar Cycloaddition Route to Fluorinated Nucleoside Analogues

**H. WOJTOWICZ-RAJCHEL** [(a)]*, **E. MUSZYNKSKA** [(a)], **H. KORONIAK** [(b)]

[(a)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY - POZNAN (POLAND)
[(b)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* wojto@amu.edu.pl

Isoxazolidinyl nucleosides represent a relatively new and challenging class of potential antiviral agents. The 1,3-dipolar cycloaddition is one of the most useful and convenient tools for the preparation of N,O-heterocyclic analogues of the natural nucleosides [1]. These compounds are generally obtained from the reaction between nitrones and N-vinyl derivatives of purine and pyrimidine nucleobases. Some of these nucleosides have been found to show high cytostatic activity.

Fluorinated analogues of biologically important compounds have aroused much interest because of their unique properties which are important for medicinal chemistry and biochemistry. In the course of our work on fluorinated derivatives of nucleobases [2,3], we would like to report our results on the synthesis of fluorinated isoxazolidine analogues of nucleosides. A new class of analogues was synthesized by the direct 1,3-dipolar cycloaddition of N-β-fluoro-β-trifluoromethylenamines of nucleobases as dipolarophiles and N-protected nitrones. The cycloaddition reactions were completely regio- and diastereospecyfic. Reactions carried out on the pure E and Z stereoisomers of corresponding enamines led to two pure diastereoisomers respectively (Figure 1).

Some unexpected additional aspects relating to the competitive reactions and the stereochemistry of some products will be shown at the presented poster.

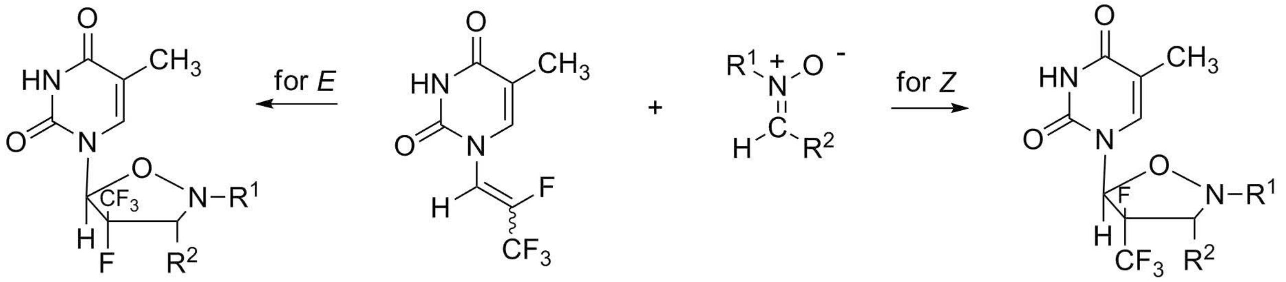

*Figure 1*

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## P1.31

# Synthesis and ring opening of α-monofluorinated β,γ-epoxy phosphonate derivatives

**M. RAPP** [(a)]*, **A. WITKOWSKA** [(a)], **K. MARGAS** [(a)], **H. KORONIAK** [(a)]

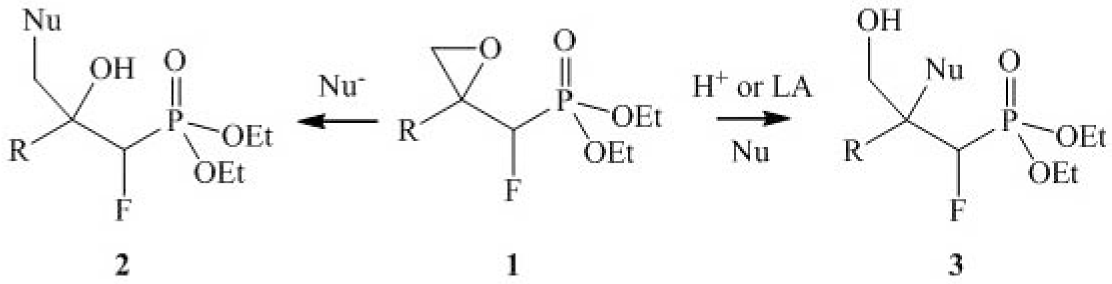
[(a)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* magdrapp@amu.edu.pl

Fluorophosphonates, considering the acidity and a steric impact, can be used as non hydrolysable and stable mimics of naturally occurring phosphates.[1] Due to their properties, the synthesis of α-monofluoromethylene phosphonates have been followed by the biological activity studies concerning some phosphatases and kinases inhibitions, between the others.[2] Based on known biological activity of aminophosphonates especially in osteoporosis treatment, the synthesis of their fluorinated counterparts have been planned.[3] Our research has focused on epoxidation of α-monofluoro-β-ketophosphonates and subsequent oxirane 1 ring opening by different nucleophiles (e.g. primary and secondary amines, azide, halide), yielding 2 or 3. The stereo- and regiochemistry of those reactions will be also discussed.

We anticipate that the resulting fluorinated hydroxy phosphonates analogues will display some biological activity.

Acknowledgments: The research was supported by Wroclaw Research Centre EIT+. BioMed (POIG.01.01.02-02-003/08)



R = Ph, Me, Bn

*Fig.1*

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## P1.32

# Exploring the chemical nature of Meerwein´s catalytic active $BF_3$ – carboxylic acid adducts

**S. PARIZEK** [(a)]*, **W. FRANK** [(a)]

[(a)] HEINRICH-HEINE-UNIVERSITäT DüSSELDORF, INSTITUT FüR ANORGANISCHE CHEMIE UND
STRUKTURCHEMIE - DÜSSELDORF (GERMANY)

* sven.parizek@uni-duesseldorf.de

Products of the reaction of boron trifluoride with carboxylic acid or anhydride have been known since the first reports by Meerwein et al. in 1927 [1] and by Bowlus et al. in 1931 [2]. These compounds offer multiple applications as reagents and catalysts in synthesis, often excelling pure $BF_3$ or other adducts in reactivity [3,4]. Examples are the oligomerization of olefins [5], Fries-rearrengements [4] or acylations [6]. Accordingly, the structure and bonding of such compounds are of particular interest.

Using inert low-temperature preparation and crystallisation techniques [7], it was possible to determine the structures of $BF_3$ – acetic acid (1/1) (1) and the product of the reaction of boron trifluoride with acetic anhydride (2) and to get additional analytic results of $BF_3$ – acetic acid (1/2). All products were synthesized by the direct action of gaseous boron trifluoride on the liquid reactants.

1 crystallizes in the monoclinic space group $P\ 2/c$ with lattice parameters of $a$ = 9.756(20) Å, $b$ = 7.8800(16) Å, $c$ = 13.1780(26) Å, $\beta$ = 101.98(3)° and Z = 8. The boron trifluoride coordinates to the carbonylic oxygen of the acetic acid, resulting in a distorted tetrahedral coordination of the boron atom. The adduct forms dimers as shown in Fig. 1 a). 1 is sensitive to water and fumes when exposed to air. Melting starts at about 35 °C.

2 crystallizes in the orthorhombic space group $Pna2_1$ with lattice parameters of $a$ = 10.380(2) Å, $b$ = 7.6356(15) Å, $c$ = 11.103(2) Å and Z = 4. The crystals are formed by molecules as shown in Fig. 1 b). In comparison to 1 the crystals are much more stable when exposed to air and melt at remarkably higher temperatures (194 °C).[2]

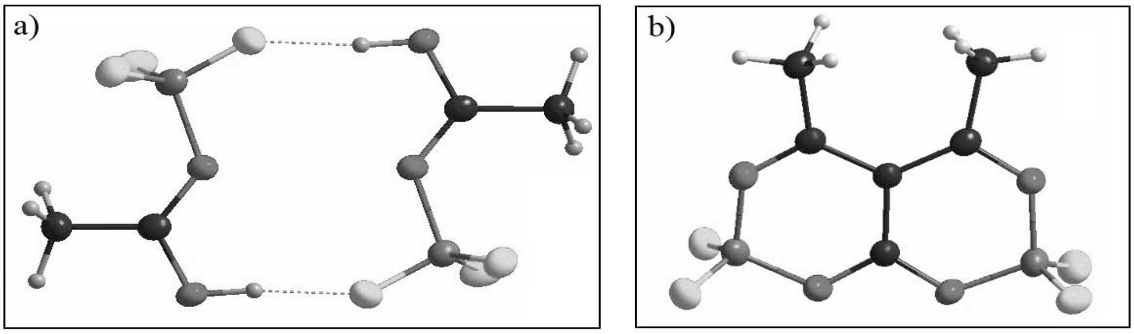

*Fig. 1: a) Dimer of 1 viewed along the crystallographic b-axis, b) Molecule of 2 in the crystal*

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## P1.33

# Synthesis and application of fluorinated β-iminophosphonates derivatives

**M. SZEWCZYK** [(a)]*, **M. RAPP** [(a)], **H. KORONIAK** [(a)]

[(a)] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* martszew@amu.edu.pl

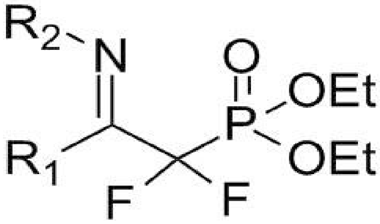

Fig. 1. *α,α-Difluorinated-β-iminophosphonate derivatives (R1= Ph, Me; R2= Bn, CH (CH3)Ph)*

Phosphate moiety is present in many biological active compounds like: ATP, NADPH, DNA. Due to hydrolysable P—O linkage in organisms, phosphonates including those containing fluorine atom(s), instead of phosphate group has been applied [1]. The specific properties as high electronegativity, strong C-F bond and small size of fluorine, usually lead to the preparation of compounds characterized by significant biological activity, good migration through lipid membranes and stability in a biological environment. Indeed, mono- or difluorinated phosphonates shows many antiviral and anticancer properties and have got a number of applications as inhibitors, substrates for an enzymes or drugs [2]. This led us to synthesis of α,α-*gem*-difluorinated-β-iminophosphonates (Fig. 1). These compounds can be used as convenient building blocks for the preparation of potential inhibitor of Cathepsine K – enzyme responsible for bone resorption and osteoporosis treatment target.

Acknowledgments: The research was supported by Wroclaw Research Centre EIT+.
BioMed (POIG.01.01.02-02-003/08)

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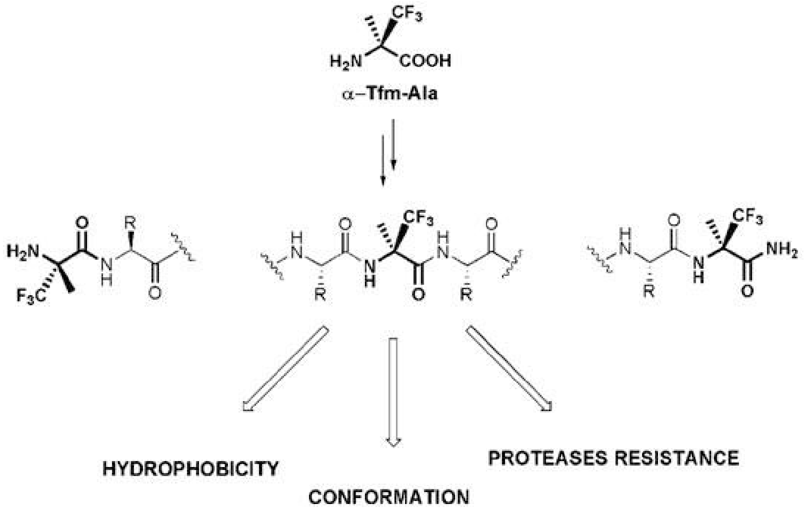
## P1.34

# Synthesis of Trifluoromethylated Tripeptides and Evaluation of their Hydrophobicity

**E. DEVILLERS** [(a)*], **J. PYTKOWICZ** [(a)], **E. CHELAIN** [(a)], **V. GASPARIK** [(a)], **T. BRIGAUD** [(a)]
[(a)] UNIVERSITE DE CERGY-PONTOISE, LABORATOIRE SOSCO - CERGY-PONTOISE (FRANCE)
* emmanuelledevillers@yahoo.fr



The incorporation of alpha-trifluoromethyl amino acids (alpha-Tfm-AAs) into peptides is susceptible to provide particular physical, chemical, and biological properties : modification of the hydrophobicity, enhanced resistance toward proteases, modification of the peptides conformation and modification of neighboring functions' pKa.[1,2,3]

In order to study the consequences of the introduction of a fluorinated amino acid in a short peptide, we synthesized several tripeptides containing alpha-Tfm-Alanine in different positions (*C*-terminal, *N*-terminal and internal). As trifluoromethyl group highly decreases the reactivity of the amine of such amino acids, their coupling in that position is a key step.[4]

We want to resume the methodological study of the coupling conditions allowing the synthesis of diverse alpha-trifluoromethylated peptides and the first hydrophobicity values we obtained from HPLC experiments.[5]

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## P1.35

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# Enantioselective Transfer Hydrogenation of $CF_3$-substituted Ketimines by Means of Chiral Phosphoric Acid

**T. AKIYAMA** [(a)]*

[(a)] GAKUSHUIN UNIVERSITY, DEPARTMENT OF CHEMISTRY - TOKYO (JAPAN)

* takahiko.akiyama@gakushuin.ac.jp

Chiral amine bearing trifluoromethyl group at alpha position is an important structural unit. Enantioselective reduction of $CF_3$ ketimine represent a useful method for the preparation of the structure in optically pure form. As part of our continued interest in the phosphoric acid catalyzed reactions, we reported transfer hydrogenation of ketimines by use of benzothiazoline as a hydrogen donor in cimbination with chiral phoshoric acid derived from (R)-BINOL[1]. We have applied the enantioselective transfer hydrogenation to the reduction of trifluoromethylated ketimines.

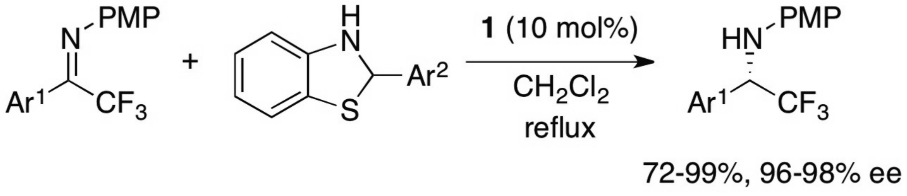
Trifluoromethylated ketimines underwent transfer hydrogenation by use of 2-(4-nitrophenyl)benzothiazoline as a hydrogen donor in the presence of 10 mol% of chiral phosphoric acid bearing 3,5-$(CF_3)_2C_6H_3$ moiety at 3,3'-position in refluxing $CH_2Cl_2$ to furnish alpha-trifluoromethylated amines in high yields and with excellent enantioselectivities[2]. Reductive amination of 2,2,2-trifluoromethylacetophenone also worked efficiently.

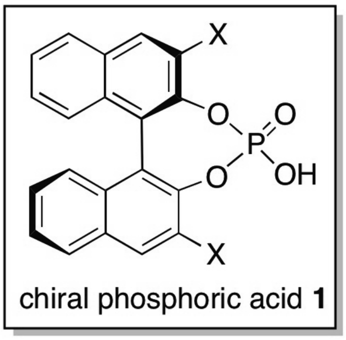
The p-methoxyphenyl (PMP) group could be oxidative cleaved by treatment with a mixture of $H_5IO_6$ and sulfuric acid to provide primary amine in high yield.

In order to demonstrate the utility of the enantioselective transfer hydrogeneation, a perfluoromethylated analogue of NPS R-568, which has been used for the treatment of hyperparathyroidism, was synthesized.

The difference of the reactivity between benzothiazoline and Hantzsch ester for the transfer hydrogenation is also discussed.

We also studied the enantioselective transfer hydrogenation of $CF_3$-substituted N-H ketimines in order to obviate the deprotection process of PMP group. The corresponding primary amines were obtained in high eantioselectivities.





chiral phosphoric acid **1**

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## P1.36

# Hydrophobicity and Helix-propensity of Fluorinated Isoleucine Variants

**S. HUHMANN** [(a)]*, **H. ERDBRINK** [(a)], **E. NYAKATURA** [(a)], **U. GERLING** [(a)], **C. CZEKELIUS** [(a)], **B. KOKSCH** [(a)]

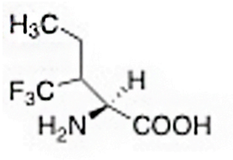
[(a)] Freie Universität Berlin, Institute of Chemistry and Biochemistry - BERLIN (GERMANY)

* susanne.huhmann@fu-berlin.de

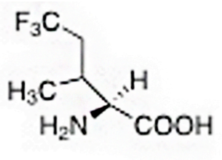
Structural modifications of peptides and proteins using non-natural amino acids provide the opportunity to improve their biophysical and pharmaceutical properties as well as to modulate their biological activity. The successful application of fluorine in the development of pharmaceuticals also motivates the interest in using this halogen as a heteroatom in amino acids.[1] Substituting side chain hydrogen atoms of hydrophobic amino acids with fluorine enhances their hydrophobicity. Understanding the hydrophobicity of amino acid side chains is a fundamental aspect of biology, since hydrophobicity is one of the main stability determinants in protein folding.

Numerous studies focus on the incorporation of fluorinated aliphatic amino acids in helical folds, even though their intrinsic tendency to adopt this structural motif (i.e. their α-helix propensity) was shown to be considerably reduced when compared to their canonical analogues.[2,3] Since, the relationship of side chain hydrophobicity and α-helix propensity is of crucial importance for the overall stability of helical assemblies, we continue to study these properties of fluorinated amino acids.

To this end, we generated two isomers of Fmoc protected fluorinated Ile (4'-$F_3$TfIle[2] and 5-$F_3$TfIle) in enantiomerically pure forms and studied their hydrophobicity in a RP-HPLC assay. Moreover, we incorporated these building blocks in an α-helix forming model peptide which was developed by Cheng et al. to study helix propensities.[3] We find that a close proximity of the voluminous $CF_3$-group to the peptide backbone results in a complete loss of α-helix propensity, while the fluorination of isoleucine's γ-methyl group still retains helicity of the model peptide.



4'-$F_3$TfIle



5-$F_3$TfIle

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## P1.37

# The Electrophilic Fluoroalkylation of Ni(II) N-Confused Porphyrins with Fluoroalkylarylsulfonium Salts

**G. ZONG** [(a)]*, **F. HAO** [(a)], **H.W. JIANG** [(a)], **Z. ZHOU** [(a)], **R. DU** [(a)], **Q. CHEN** [(a)], **J. XIAO** [(a)]

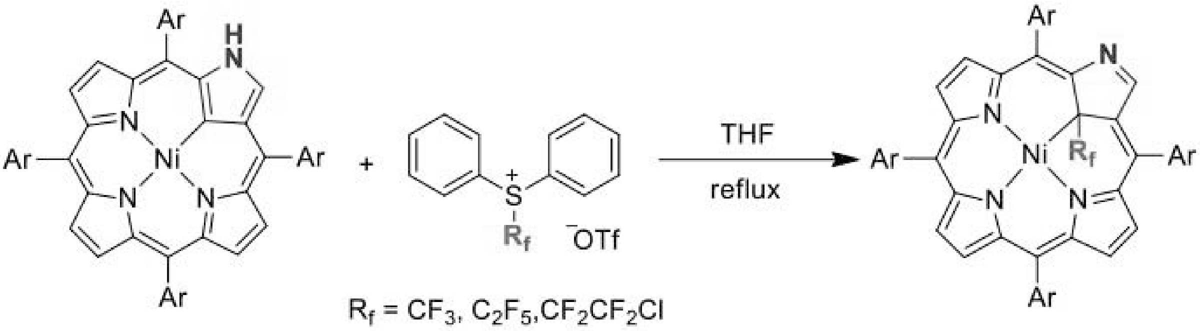
[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)

* gqzong@sioc.ac.cn

The fluorinated porphyrin derivatives have been widely investigated because of their unique properties[1]. They are considered as potential candidates for the photodynamic therapy (PDT) and have been proved to be effective catalyst. Besides, the fluorine-containing porphyrins have also been applied in semiconductor materials, molecular devices and so on. However, the synthesis of fluorine-containing metalloporphyrins was very challenging. The traditional method, starting from fluorinated pyrrole or aldehyde, usually took several steps, leading to very low yields.

Recently, we investigated the synthesis of fluoroalkylarylsulfonium salts and their electrophilic fluoroalkylations[2]. Considering the electronic properties of N-confused porphyrins, we assumed that the electrophilic fluoroalkylation of Ni(II) N-confused porphyrins with fluoroalkylarylsulfonium salts would similarly happen.

Experimental studies showed that Ni(II) N-confused porphyrins, treated with fluoroalkylarylsulfonium salts, can undergo an electrophilic fluoroalkylation at the inner 21-C position, leading to 21-fluoroalkylated Ni(II) N-confused porphyrins. The interesting substitution effect at the para-position of the phenyl moiety was found. Further studies on the properties and applications of fluoroalkylated N-confused porphyrins are now under way.



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## P1.38

# Strategic Approach to Synthesis of 2,3,5,6-(Tetrakis)trifluoromethyl-4-Chloro Pyridine and its Derivatives

**S. SERGEEV** [(a)], **V. PETRIK** [(a)*]

[(a)] CHEMTAURUS GMBH - BREMEN (DEUTSCHLAND)

* vitpetrik@yahoo.com

**In memory of Alexander Kolomeitsev**

Pyridines are an important class of nitrogen-containing heterocycles, many of which are potential drug candidates, and also can be used as crop protection products and compounds for material science [1, 2]. At the same time, fluoroorganic compounds have received much attention, since the inclusion of fluorine-containing groups into organic molecules leads to a drastic change in its physical, chemical and biological properties [3]. The interest to fluorinated pyridines has precipitously increased with many important synthetic attainments having been reported in the last two decades [4].

In this presentation we would like to introduce an efficient method for the synthesis of 2,3,5,6-(*tetrakis* )trifluoromethyl-4-chloro pyridine 1. The approach involves four steps and allows synthesize of pyridine 1 in large-scale amounts as well in the laboratory conditions.

The synthetic capability of 2,3,5,6-(*tetrakis*)trifluoromethyl-4-chloro pyridine 1 will also be presented.

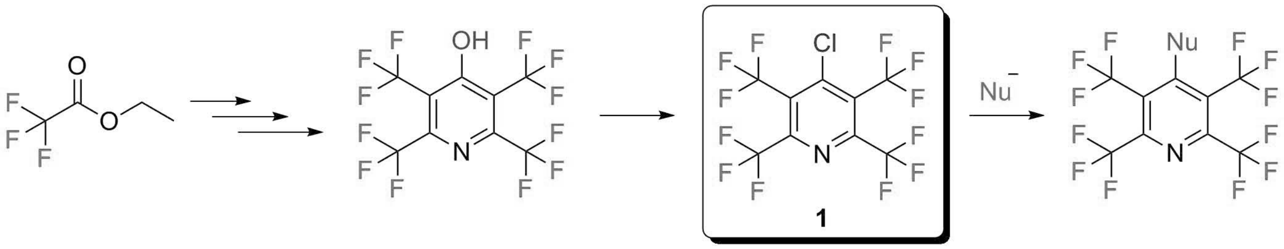

Figure 1. 2,3,5,6-(*Tetrakis*)trifluoromethyl-4-chloro pyridine **1** and its derivatives

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## P1.39

# Organocatalytic Reactions of α-Trifluoromethylated Compounds with Alkenes

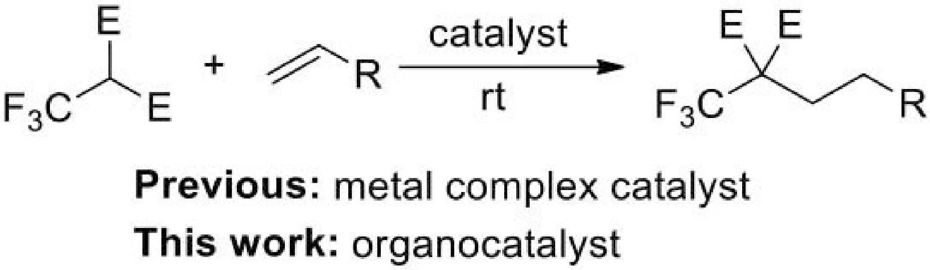
**Q. WANG [(a)], F. HUAN [(a)], J. XIAO [(a)], M. GAO [(a)], X. YANG [(b)], S.I. MURAHASHI [(c)], Q. CHEN [(a)], Y. GUO [(a)]***

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)
[(b)] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology - SHANGHAI (CHINA)
[(c)] Department of Chemistry, Okayama University of Science - OKAYAMA (JAPAN)

* yguo@sioc.ac.cn

Fluorinated compounds have aroused extensive interest because of the unique properties brought by fluorine to organic molecules. One of synthetic challenges on organofluorine chemistry is the β-defluorination when an anion is generated α to a $CF_3$ group. The $CF_3$ carbanion is easy to defluorinated to give an alkene and hard to react with an electrophile and the lifetime of the anion can be increased when stabilized by an electron-withdrawing group.[1]

In 2009, we reported that $CF_3$-containing esters ($CF_3CHR^1CO_2Me$) reacted with acrylonitrile under the catalysis of $IrH_5(iPr_3P)_2$, giving adducts in good yields and proposed a C-H activation mechanism.[2] Interestingly, when we did some control experiments to exclude some reaction pathways, we found $i$Pr$_3$P can *also* promote the reaction although in a much less efficiency. This discovery forced us to find out a non-metal catalysis (Scheme 1), which was expected to be complementary and with a wide reactant scope. Herein, we wish to report our recent research of organocatalytic reactions of α-trifluoromethylated compounds with alkenes.



*Scheme 1. Michael reactions of $CF_3$-containing ester by organocatalyst*

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## P1.40

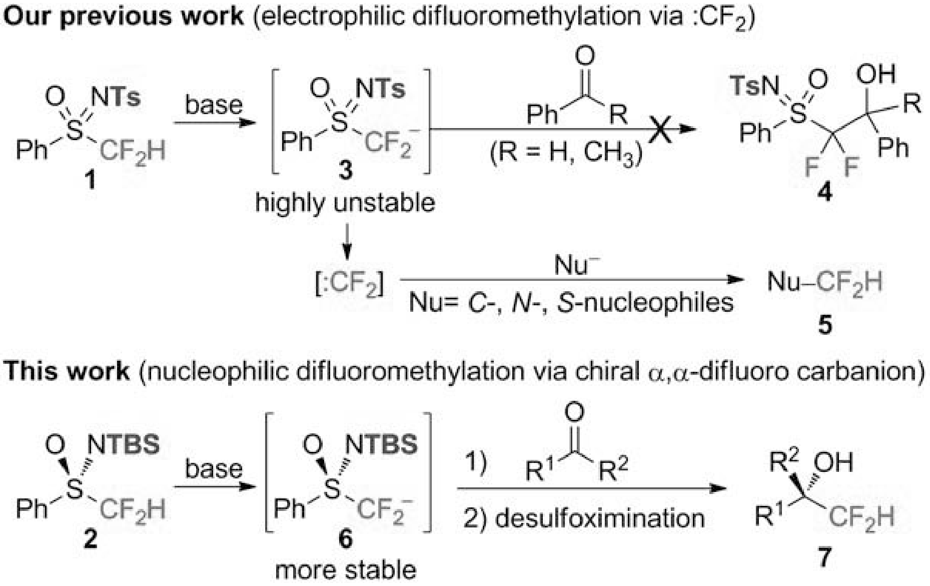
# Tuning the Reactivity of Difluoromethyl Sulfoximines from Electrophilic to Nucleophilic: Stereoselective Nucleophilic Difluoromethylation of Aryl Ketones

**X. SHEN** [(a)], **W. ZHANG** [(a)*], **C. NI** [(a)], **J. HU** [(a)*]

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)

* weizhang83@sioc.ac.cn
jinbohu@sioc.ac.cn

A stereoselective synthesis of enantiomerically enriched difluoromethyl tertiary alcohols by tuning the reactivity of difluoromethyl sulfoximines from electrophilic to nucleophilic difluoromethylating agents is reported (Fig. 1).The key feature of this chemistry is the diastereoselective addition of the difluoromethyl sulfoximine to the prochiral carbon of the ketone. The present method was used to prepare enantiomerically enriched difluoromethyl secondary alcohols and difluorinated analogues of the natural products gossonorol and boivinian B, demonstrating the potency of the method. [1, 2]



*Tuning the Reactivity of Difluoromethyl Sulfoximines from Electrophilic to Nucleophilic*

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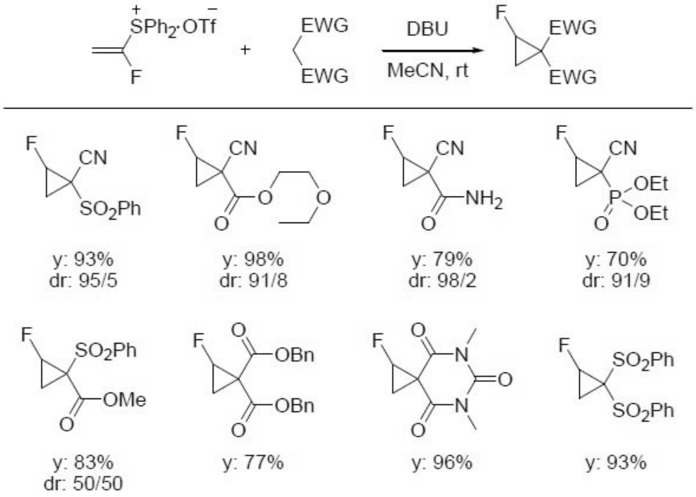
## P1.41

# Synthesis of mono-fluorinated cyclopropanes and aziridines using α-(fluorovinyl) diphenylsulfonium salt

**<u>K. HIROTAKI</u> [a]***, **T. HANAMOTO [a]**

[a] SAGA UNIVERSITY, DEPARTMENT OF CHEMISTRY AND APPLIED CHEMISTRY - SAGA (JAPAN)

* 11634014@edu.cc.saga-u.ac.jp



Monofluorinated cyclopropanes have recently drawn much attention due to their wide utility as precursors for medicinal and functional materials. However, the facile synthesis of such molecules using annulation reactions is scarce. We considered that these molecules should be accessible from appropriate active methylene compounds and the monofluorinated vinyl sulfonium salt under mild conditions on the basis of our recent finding about β-(trifluoromethyl)vinyl sulfonium salt. In this poster presentation, we disclose our recent finding about the first preparation of (α-fluorovinyl) diphenylsulfonium salt and the facile synthesis of mono-fluorinated cyclopropanes and aziridines.

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## P1.42

# Synthesis of new [18F]fluoro sugar prosthetic groups to radiolabelled peptide for PET imaging

**S. LAMANDE-LANGLE [a]*, C. COLLET [b], R. HENSIENNE [a], F. CHRÉTIEN [a], F. MASKALI [b], P.Y. MARIE [b], G. KARCHER [b], Y. CHAPLEUR [a]**

[a] Université de Lorraine-CNRS, UMR 7565 SRSMC - VANDOEUVRE LES NANCY (FRANCE)
[b] NancycloTEP - VANDOEUVRE LES NANCY (FRANCE)

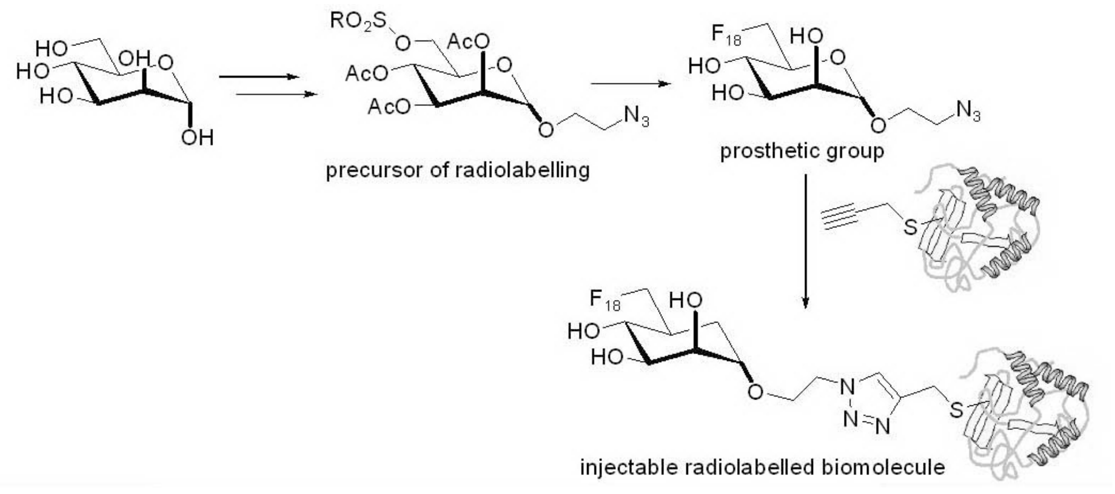
* sandrine.langle@univ-lorraine.fr

Following and monitoring evolution of a molecule in the body with PET imaging[1] requires the availability of this molecule radiolabelled with a positron-emitting as fluorine-18 (18F). The 18F labelling of biomolecules (proteins, peptides or oligonucleotides) has been used for many years[2]. However, the sensitivity of these macromolecules does not allow their radiolabelling by direct incorporation of 18F. Solution is to use a prosthetic group, an easily radiolabelled small molecule, subsequently coupled to the biomolecule.

We therefore propose to develop and use new more simple and easily accessible prosthetic groups. They will also permit the efficient radiolabelling with fluorine-18.The use of sugar as prosthetic group is innovative and would improve the bioavailability of protein. The sugar must have a good leaving group thus allowing easy substitution by fluorine-18. For coupling the prosthetic group with the biomolecule we use a Huisgen cycloaddition[3].

Some model peptide are used (i.e. RGDC and Gluthation) containing a cysteine residue. The high nucleophilicity of the thiol function can be exploited to prepare *S*-alkylated derivatives.

The synthesis of suitable precursors of these prosthetic groups and the radiolabelling of some model peptide will be present[4]. PET images will be discussed.



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P1.43

# Assessment of the Potential of the Fluoride and Chloride Salts for CSP

**B. KUBIKOVA** [(a)]*, **N. PFLEGER** [(b)], **T. BAUER** [(b)]

[(a)] INSTITUTE OF INORGANIC CHEMISTRY, SAS, DEPARTMENT OF MOLTEN SALTS - BRATISLAVA (SLOVAKIA)
[(b)] INSTITUTE OF TECHNICAL THERMODYNAMICS, GERMAN AEROSPACE CENTER - KOLN (GERMANY)
[(b)] INSTITUTE OF TECHNICAL THERMODYNAMICS, GERMAN AEROSPACE CENTER - STUTTGART (GERMANY)

* blanka.kubikova@savba.sk

As the commercially used salts as thermal energy storage materials are not suitable so far for the applications at high temperatures due to their thermal instability over 650°C, presented work was focused on the assessment of the potential of the fluoride and chloride salts for concentrated solar power (CSP). For this application materials should possess several properties as suitable melting temperature and congruent melting, high specific heat capacity and heat conductivity, chemical and thermal stability, minimum volume changes, non-toxicity or little toxicity, availability and cheapness, compatibility with the construction material, etc. [1-2]. Alkali and alkaline earth metals of fluorides and chlorides have been taken under consideration. It is known that they are chemically stable, have demanding melting temperature (that can be decreased when mixing two or more salts together), high specific heat capacities and heat of fusion. They have low vapour pressure and melt congruently. Some of the selected salts possess also negative properties that reject them from the consideration of using them for CSP. They are toxicity, hygroscopicity and corrosion resistance of the construction materials against molten salts. These properties have been studied in detail. It has been found that the most fluoride salts are toxic and the disadvantage of some of the chloride salts is their high hygroscopicity. Concerning the corrosion resistance of the construction materials against the halogen salts, there are possibilitiesof of suitable construction materials, but they are expensive. In order to decrease the initial costs, mixing of chlorides with other salts, e.g. sulphates and/or carbonates has been reviewed and the stability of the mixtures has been investigated.

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**P1.44**

# Versatile preparations of perfluoroalkylated bis-sulfilimines and bis-sulfoximines

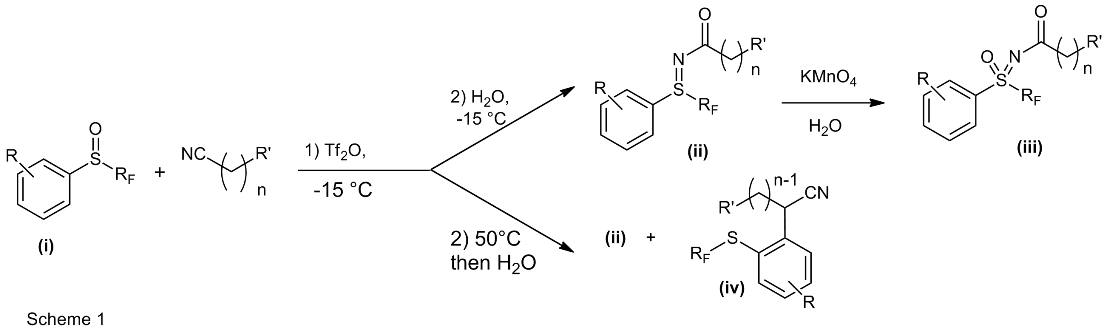
**B. PEGOT** [(a)]*, **C. URBAN** [(a)], **P. DITER** [(a)], **E. MAGNIER** [(a)]

[(a)] INSTITUT LAVOISIER VERSAILLES, UMR 8180 - ECHO ÉQUIPE FLUOR, UNIVERSITÉ DE VERSAILLES - VERSAILLES (FRANCE)

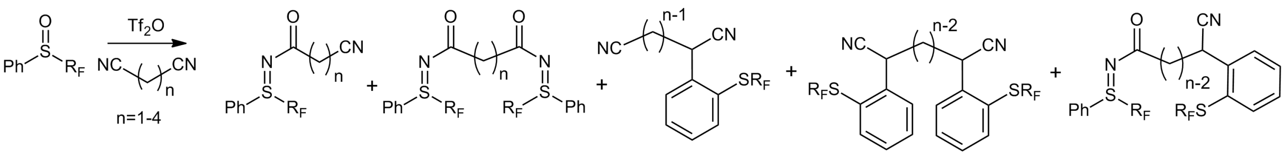
* bruce.pegot@uvsq.fr

The major progress recently realized in the domain of electrophilic introduction of fluoroalkylated groups are possible thanks to the availability of various fluorinated reagents and more particularly the recent family of sulfoximine.[1] Our research group has recently described a flexible and versatile methodology which allowed the preparation of a wide range of perfluoroalkyl sulfur compounds started with common simple perfluoroalkyl sulfoxides (i) (Scheme 1).[2] At low temperature, hydrolysis afforded the acylsulfilimines (ii). Heating of the reaction mixture before introduction of water led this time to a mixture of sulfilimines (ii) and perfluoroalkyl thioethers (iv).[3] Our methodology is ecofriendly since it is using any solvent, a nontoxic oxidizing agent and furthermore allows a great structural flexibility. Variations of the aromatic substituents, of the nitrile and of the fluorinated chain are also feasible.

As part of our program devoted to the development of new electrophilic perfluoroalkylating reagents and new electronwithdrawing groups, we were really intrigued by the reactivity of dinitriles with sulfoxides. The presence of two reactive sites would deeply enhance the structural diversity providing that we could be able to control the selectivity of our transformations. The number of compounds formed would be indeed, not only dependent of the reaction conditions but also of the length of the tether between the two nitriles moieties (scheme 2).



Scheme 1



Scheme 2

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## P1.45

# An improved synthesis of the 2,3,4-trideoxy-2,3,4-trifluoro hexose analogue of D-glucose

**M. CORR [(a)]*, D. O'HAGAN [(a)]**

[(a)] Biomolecular Sciences Research Complex, University of St Andrews - ST ANDREWS (UNITED KINGDOM)

* mc410@st-andrews.ac.uk

Substitution of hydroxyl groups by fluorine to give the corresponding deoxofluorosugars is a common modification in carbohydrate chemistry [1,2]. Introduction of fluorine into a sugar molecule provides a powerful sensor for investigation of carbohydrate mechanisms, by $^{19}$F-NMR with no background signal in biological systems [3]. We have previously reported the synthesis of the 2,3,4-trideoxy-2,3,4-trifluoro hexose analogue of D-glucose 1 (Figure 1) [4,5] and studied its transport across the membranes of red blood cells [5]. In an extension of this program, we sought to develop a more efficient synthesis of trifluoroglucose 1, in order to obtain sufficient material for further investigation into enzymatic systems.

The poster will present an improved synthesis of the 2,3,4-trideoxy-2,3,4-trifluoro hexose analogue of D-Glucose 1. The previous synthesis [4,5] suffered from fluorination reactions that gave rise to multiple regioisomers and diastereoisomers, resulting in laborious purification by silica gel chromatography and low yields as a consequence. The improved synthesis was designed such that only a single diastereoisomer was produced in each fluorination reaction, leading to an improved overall yield and easier isolation.

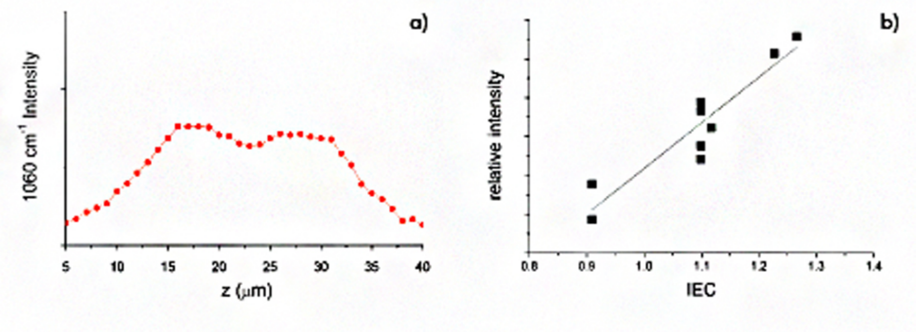

*Figure 1. Tirfluoroglucose 1 and X-ray crystal structure of the beta-anomer [5].*

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## P1.46

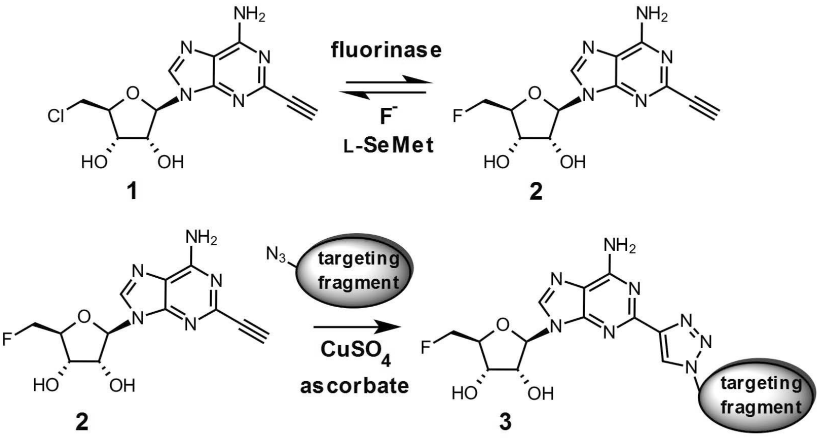
# Extending the Synthetic Utility of the Fluorinase for Positron Emission Tomography using Click Chemistry

**S. THOMPSON** [a]*, **S. MCMAHON** [b], **C. DREHER** [b], **J. NAISMITH** [b], **D. O'HAGAN** [b]

[a] Biomolecular Sciences Research Complex, University of St Andrews, DAVID O'HAGAN GROUP - ST ANDREWS (UNITED KINGDOM)
[b] Biomolecular Sciences Research Complex, University of St Andrews - ST ANDREWS (UNITED KINGDOM)

* st59@st-andrews.ac.uk

Positron emission tomography (PET) has emerged as an invaluable tool for molecular imaging in the clinic. This technique allows for the visualisation of metabolic processes through the interaction of a radiotracer and a metabolic target, with applications in neurology, cardiology and oncology. The short lived nature of PET radioisotopes, e.g $^{18}F$ ($t_{1/2}$ 110 min), requires short, elegant syntheses of radiotracers, compatible with commonly available radionucleide production methods.[1]



*Scheme 1: Enzymatic conversion of ClDEA (1) to FDEA (2), and subsequent "Click" reaction.*

The fluorinase (from soil bacterium *Streptomyces cattleya*) offers an enzymatic route to novel radiotracers. Uniquely, the fluorinase catalyses the formation of a C-F bond from aqueous fluoride, the form of fluoride most commonly produced from cyclotron radionuclide production facilities. Using *S* -adenosylmethionine (SAM) as an electrophile, the fluorinase catalyses an $S_N2$-like reaction with $F^-$ to produce 5′-fluoro-5′-deoxyadenosine.[2,3]

This study describes the synthesis of a novel substrate for the fluorinase which carries an acetylene substituent. Synthesis of ClDEA (1) and a synthetic reference compound of the anticipated fluorinated product FDEA (2), will be described.

In the presence of aqueous fluoride ($^{19}F^-$) and L-selenomethionine, the fluorinase efficiently converted ClDEA (1) to FDEA (2) (Scheme 1), confirmed using a combination of HPLC, LCMS and comparison to synthetic standards. Enzymatically synthesised FDEA (2) was also shown to undergo rapid coupling to an azide-bearing RGD peptide using the copper catalysed Huisgen 1,3-dipolar cycloaddition (a “click” reaction). With $^{18}F^-$ as the fluoride source, the approach will provide access to a novel class of radiotracer (3) for targeted imaging of cancers or other metabolic processes of interest.

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## P1.47

# Direct Electrophilic Trifluoromethylation of Nitrogen Containing Arenes Using a Hypervalent Iodine Reagent

**N. FRUEH** [(a)]*, **A. TOGNI** [(a)]
[(a)] ETH ZÜRICH, LAC - ZÜRICH (SWITZERLAND)
* frueh@inorg.chem.ethz.ch

The synthetic strategies towards N-trifluoromethylated organic compounds consist mainly of functional group interconversions [1] or oxidative desulfurization-fluorination. [2] The direct electrophilic trifluoromethylation of hard nucleophiles remains a challenge.

As shown in Figure 1 reagent 1 undergoes a novel acid catalyzed Ritter type reaction in acetonitrile with an azole (2) during which 2 is converted to the N-substituted *N*-trifluoroimidoyl derivative. [3] A variety of azoles, such as benzotriazole, indazole, and substituted pyrazoles were subjected to the optimized reaction conditions and the trifluoromethylated products were obtained in moderate to good yields. Thorough structure elucidation was carried out both by heteronuclear 2D NMR experiments and by X-Ray crystallography. Quantum chemical calculations propose either a transition metal like mechanism or the formation of a nitrilium ion that is rapidly trapped by the nucleophile. [4] These proposed mechanisms were supported by $^{19}F$ NMR reaction monitoring.

As a byproduct in the above mentioned reaction N-trifluoromethyl benzotriazole was observed. Reaction optimization for benzotriazole as a model substrate led to the formation of the desired product in excellent yield. These optimized reaction conditions that consist of in situ silylation of the substrate followed by acid catalyzed trifluoromethylation were applied to a variety of substituted azoles such as indazole, pyrazoles, and triazoles (Figure 1). Full characterization of the products was carried out using heteronuclear 2D NMR spectroscopy and X-Ray spectroscopy. [5]

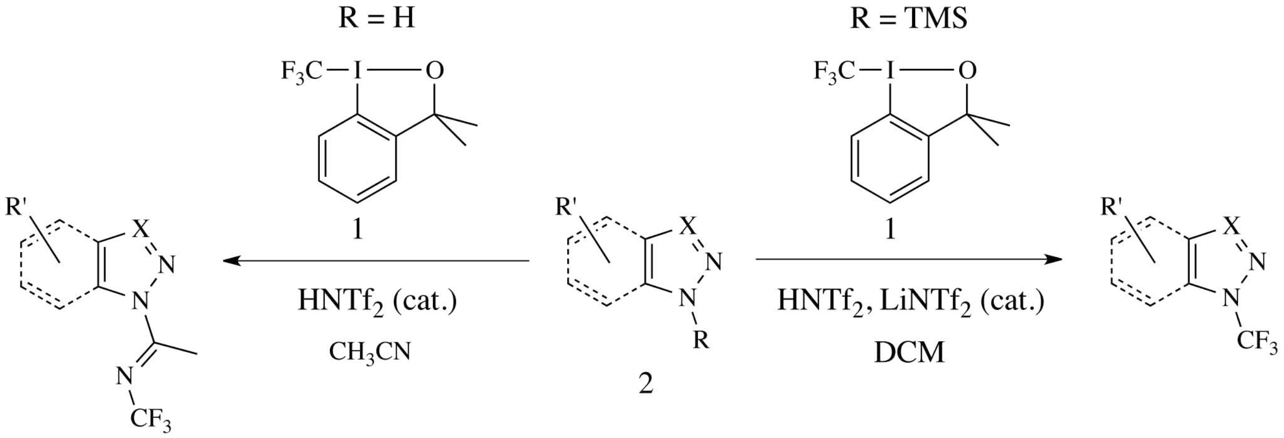

*Fig. 1. Direct electrophilic trifluoromethylation of azoles.*

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[5] K. Niedermann, N. Früh, R. Senn, B. Czarniecki, R. Verel, A. Togni, *Angw. Chem. Int. Ed.*, **51** (2012) 6511.

## P1.48

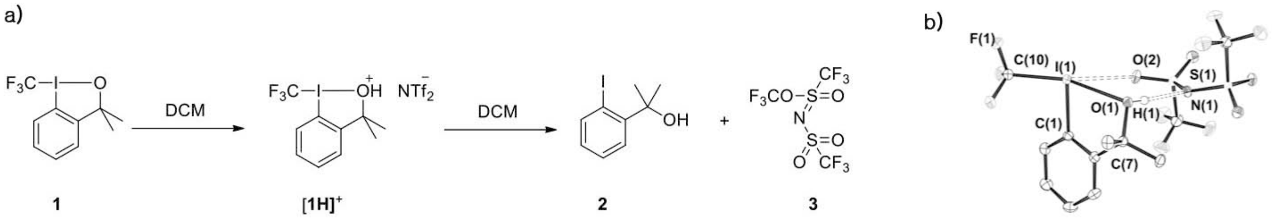
# Investigations on Activated Hypervalent Iodine Trifluoromethylation Reagents

**E. OTTH** [(a)]*, **A. TOGNI** [(b)]

[(a)] ETH ZURICH, LAC - ZURICH (SWITZERLAND)
[(b)] ETH ZURICH, DEPARTMENT OF CHEMISTRY - ZURICH (SWITZERLAND)

* elisabeth.otth@inorg.chem.ethz.ch

We have contributed to the field of electrophilic trifluoromethylation with the development of hypervalent iodine reagent 1, that since its first report has been shown to display good to excellent reactivity towards a plethora of nucleophiles.[1] Furthermore, we have observed that acids catalyse various of these electrophilic trifluoromethylation reactions by activating the reagent via protonation to the iodine-bound oxygen atom and thus weakening the I-$CF_3$ bond. This has been indicated by a strong low field chemical shift of the reagent by $^{19}F$ NMR spectroscopy and could recently be shown in the solid state by X-ray crystallography of the corresponding $BArF_{24}$-, $BF_4$- and $NTf_2$-compounds (Fig. 1) whereby the latter ($[1H]^+$) can be easily prepared and isolated from equimolar solutions of 1 and $HNTf_2$ and could be fully characterized (Fig.1). Moreover, it has been observed that $[1H]^+$ will decompose in solution to give the oxygen trifluoromethylated compound 3 that is easily identified by its characteristic $^{19}F$ NMR spectrum. The results of kinetic investigations of this decomposition reaction will be presented.



*a) Synthesis and decomposition of the HNTf2 salt of 1 b) ORTEP drawing*

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## P1.49

# Synthesis of *syn*-hexafluoroalkane

**N. AL-MAHARIK** [(a)]*

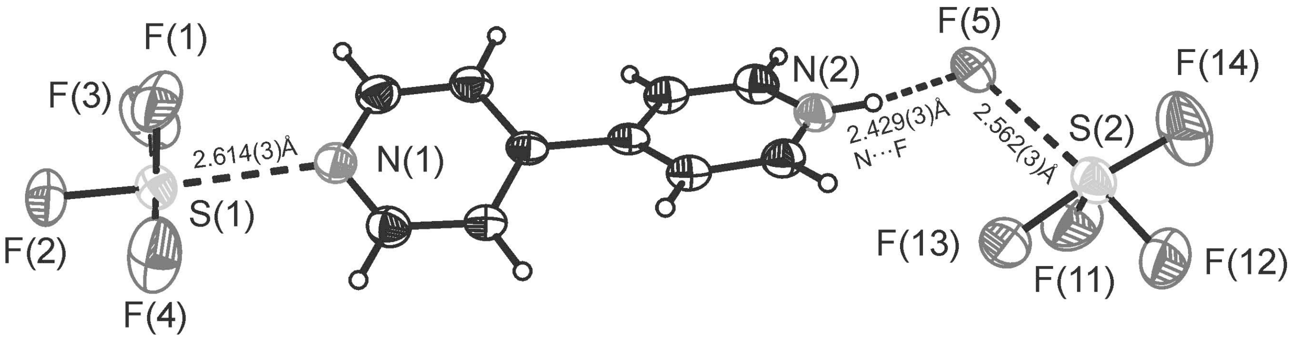
[(a)] UNIVERSITY OF ST ANDREWS, SCHOOL OF CHEMISTRY - ST ANDREWS (UK)

* na10@st-andrews.ac.uk

Several acyclic alkanes carrying three,[1,2] four,[1,2] five[1-3] and six[1,2,4] vicinal fluorine atoms as single stereoisomers have been previously prepared in our laboratory in order to provide insights into the influence of the C-F bond in determining alkyl-chain confirmations. It was found that the all-*syn* arrangement of fluorine atoms in the hexafluoro alkane 1a has a helical twist as a result of the stereoelectronic preference to avoid 1,3-C-F dipolar repulsions. Additionally, the twisted alignment is also reinforced by weaker hyperconjugative interactions leading to vicinal *gauche* C-F orientations. By contrast, the configuration of C-F bonds in the diastereoisomer 1b, which does not have any 1,3-C-F repulsive interaction, allows the molecule to adopt an anti-zigzag carbon-chain conformation. Tetrafluoroalkane 2 with an insulating ethylene linkage between the *gauche* vicinal fluorines adopts an extended zigzag conformation.

Continuing our previous work, we sought to prepare a *syn*-hexafluoroalkane with an insulating ethylene linkage in order to investigate the influence of the ethylene linkage on the conformation.

The total synthesis of the *syn*-hexavicinal fluoroalkane 4 starting from cyclohexyl carbaldehyde 3 will be presented.



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[1] D. O'Hagan, *J. Org. Chem.*, **77** (2012) 3689 -3699.
[2] N. Al-Maharik,D. O'Hagan, *Aldrichimica Acta,* **44**, (2011) 65-75.
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## P1.50

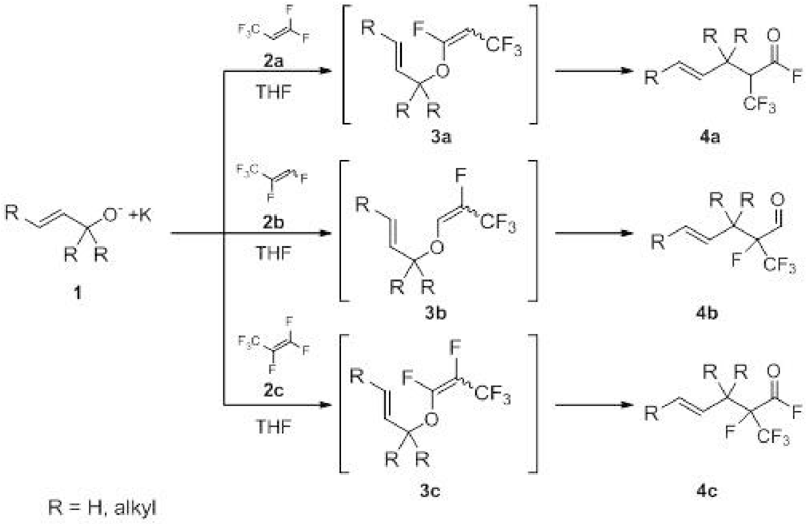
# Claisen rearrangement of fluorinated allyl-vinyl ethers

**B. MARCINIAK** [a]*, **M. RAPP** [b], **H. KORONIAK** [b]

[a] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY - POZNAN (POLAND)
[b] ADAM MICKIEWICZ UNIVERSITY, FACULTY OF CHEMISTRY, DEPARTMENT OF SYNTHESIS AND STRUCTURE OF ORGANIC COMPOUNDS - POZNAN (POLAND)

* barmar@amu.edu.pl

Sigmatropic rearrangements are very powerful tools in hands of organic chemists. They allow transition of multiple bonds and transformation of functional groups in molecules in very organized and convenient way. Claisen rearrangement of fluorinated allyl-vinyl ethers [1] results in obtaining α-trifluoromethyl-γ,δ-unsaturated carbonyl compounds 4. Depending on the fluorinated olefin used for ether generation (1,1,3,3,3-pentafluoropropene 2a, 1,2,3,3,3-pentafluoropropene 2b or hexafluoropropene 2c), aldehydes 4b or carbonyl fluorides 4a, 4c are obtained. Reaction performed on various primary, secondary and tertiary allyl alcohols 1 can give rise to very interesting substrates for unsaturated carbonyl derivatives e.g. carboxylic acids, esters and amides.



*General scheme of Claisen rearrangement of fluorinated allyl-vinyl ethers*

Although Claisen rearrangement of fluorinated ethers derived from simple allyl alcohols occurs already in -30°C, our recent research has proven that bulkier alcohols e.g. furanoses derivatives, instead of rearangement products, form stable fluorinated allyl-vinyl ethers.

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## P1.51

# Ion Mobility and Phase Transitions in Crystal Phases of Heptafluorodiantimonates $MSb_2F_7$ (M = K, Cs, $NH_4$) and $Cs_{(1-x)}M'_xSb_2F_7$ (M´ = K, $NH_4$) According to NMR and DSC Data

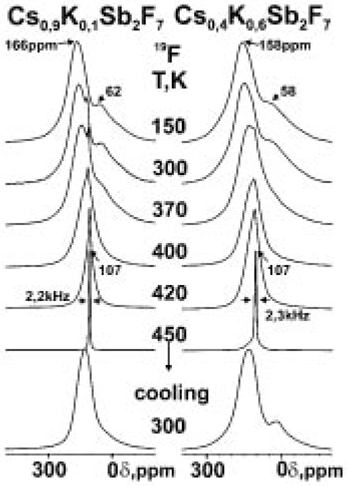
**V. KAVUN [a], L. ZEMNUKHOVA [b], M. POLYANTSEV [b], V. KHARCHENKO [c]***

[a] Institute of Chemistry, FEB RAS, NMR LAB. - VLADIVOSTOK (RUSSIA)
[b] Institute of Chemistry, FEB RAS - VLADIVOSTOK (RUSSIA)
[c] Institute of Chemistry, FEB RAS, LABORATORY OF ESQCS - VLADIVOSTOK (RUSSIA)

* vikharchenko@gmail.com

The systems based on antimony fluoride are known to show high ionic conductivity [1, 2]. Due to essentially covalent character of Sb–F bonds in $SbF_n$ coordination polyhedra and relatively long F–F interionic distance, complex fluoroantimonates are able to form a network structure with large open channels being suitable for ion transport. It appears interesting to compare properties of model heptafluorodiantimonate compounds with homo- and heteroatomic cation sublattice.

The ion mobility and phase transitions (PTs) of potassium, ammonium and cesium fluoroantimonates(III) ($KSb_2F_7$, $NH_4Sb_2F_7$ and $CsSb_2F_7$) and compounds of variable composition $Cs_{(1-x)}M_xSb_2F_7$ (M = K, $NH_4$; $0.1 \le x \le 0.6$) were studied in this work.



*19F NMR spectra of the studied compounds at different temperature*

Analysis of the shape (Fig.1) and the second moment of $^{19}F$ NMR spectra allowed revealing various types of motions in the fluorine subsystem. In the temperature range 150–490 K the type of ion motions changes in the fluoride sublattice of the studied compounds: a rigid lattice → local motions (reorientation of $SbF_n$ groups) → translational diffusion of fluorine ions. The dynamic state of the fluorine sublattice in $Cs_{(1-x)}K_xSb_2F_7$ compounds is governed by a number of potassium cations introduced into in the cesium subsystem. When $x < 0.2$, these compounds show higher mobility of fluorine ions than $CsSb_2F_7$ under the same conditions, and if $x > 0.4$, the dynamics of ion mobility deteriorates. Transition to a diffusion in model compounds $CsSb_2F_7$, $NH_4Sb_2F_7$, and compounds of variable composition $Cs_{0.9}K_{0.1}Sb_2F_7$, $Cs_{0.4}K_{0.6}Sb_2F_7$, and $Cs_{0.8}(NH_4)_{0.2}Sb_2F_7$ is due to PTs confirmed by NMR as well as DSC. Probability of transition of ammonium ions from isotropic reorientations to diffusion and their number depends on a sample composition

High-temperature phases formed at PTs are metastable and transforms into an initial modification with time. The transition time depends on a sample composition, a temperature of its heating and a time of a sample holding at this temperature. It was found that PTs in the crystalline phases $Cs_{(1-x)}K_xSb_2F_7$ are observed only at $x$ less than 0.65. The phase transitions in cesium – potassium and cesium – ammonium heptafluorodiantimonates with forming of high-temperature modifications are PTs to a superionic state in which the dominant form of the ion motion is diffusion of fluorine ions. This conclusion is confirmed by ionic conductivity: the high-temperature phases $Cs_{(1-x)}K_xSb_2F_7$ are superionic, their conductivity reaches $10^{-3}$ –$10^{-4}$ S/cm at temperature 463–483 K, so these systems can be considered as potential compounds for materials with high ionic conductivity.

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[2] V.Ya. Kavun, N.F. Uvarov, A.B. Slobodyuk, et al., *Rus. J. Electrochem.*, 41 (2005) 488-493.

## P1.52

# Synthesis and characterisation of nanoscopic $SrF_2$ *via* sol-gel synthesis

**L. SCHMIDT** [(a)] , **E. KEMNITZ** [(b)]*

[(a)] Humboldt-Universität zu Berlin, Department of Chemistry, DEPARTMENT OF CHEMISTRY - BERLIN (GERMANY)
[(b)] Humboldt-Universität zu Berlin, DEPARTMENT OF CHEMISTRY - BERLIN (GERMANY)

* erhard.kemnitz@chemie.hu-berlin.de

Because of its excellent optical properties *e.g.* its low refractive index ($n_D$= 1.439 @ 589 nm), the high transmission in the infrared and ultraviolet spectral range (0.13-11 µm) and the low solubility in water (120 $mg \cdot L^{-1}$) $SrF_2$ is an ideal material for optical applications and is often used as a coating material for high-quality optical windows and lenses.

Furthermore, $SrF_2$ is of significant interest in dentistry as inorganic filler in dental composites. Nanosized $SrF_2$ can improve not only mechanical and chemical properties of dental materials, but also increase the caries-inhibiting effect due to a higher and long-term fluoride release. It was previously shown that the high F release of nanocomposites was likely related to the large surface area of nanosized particles.[1]

Nanoscopic alkaline earth metal fluorides $MF_2$ (M = Mg, Ca, Sr) have been successfully synthesized *via* fluorolytic sol-gel route which was succesfully developed and established by our group.[2] The stoichiometric reaction of the metal precursor with alcoholic HF solution in an organic solvent leads to transparent $SrF_2$ sols of low viscosity. An overall characterisation of $SrF_2$ particles with various analytical methods like DLS, XRD and TEM reveals the formation and existence of $SrF_2$ sol particles of about 5 nm with large surface areas of 180 $m^2 \cdot g^{-1}$. Utilising spectroscopical and crystallographic methods (solid state NMR, XRD and WAXS) allowed us to gain more chemical and structural information during the ageing process as well as the long-time behaviour of $SrF_2$ sols.

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[2] E. Kemnitz, U.Groß, S. Rüdiger, C.S. Shekar, *Angew. Chem. Int. Ed.;* **42**, (2003), 4251.

## P1.53

# Mass-Spectrometric Study on the Occurrence of Elemental Fluorine in the Natural Mineral "Antozonite"

**P.P. SEMYANNIKOV** [(a)], **V. MITKIN** [(a)*], **F. KRAUS** [(b)], **S.V. TRUBIN** [(a)]
[(a)] NIKOLAEV INSTITUTE OF INORGANIC CHEMISTRY SB RAS - NOVOSIBIRSK (RUSSIA)
[(b)] Technische Universität München, - GARCHING (GERMANY)
* mit48@mail.ru

Over 125 years since Henry Moissan's pioneer works on the isolation of fluorine in its elemental state there was a common opinion that molecular fluorine ($F_2$) cannot exist on the Earth in its free form. Nevertheless, since 1816 some publications appeared that elemental fluorine may exist in some rare F-containing minerals, for example "antozonite" (a variant of fluorite $CaF_2$). The main reason of interest in "antozonite" was due to its strange smell, which originated when the solid mineral was crushed. Because "smell" is an organoleptic parameter, it was obviously necessary to obtain some direct confirmation of the $F_2$ presence in "antozonite". In a recent paper [1] it has been unambiguously confirmed the presence of $F_2$ in "antozonite" by solid state $^{19}$F-NMR,that showed ca. 0.5 mg/g of a gaseous substance that exhibits a chemical shift similar to that of molecular fluorine $F_2$. The aim of the present work was the continuation of the "antozonite" study by mass-spectrometry. This method has been used several times previously (Heinrich et al., 1965; Braithwaite et al., 1973; Vochten et al. 1977) to directly detect $F_2$ in the mineral, but the obtained results were very contradictory.

In our investigations a sample of "antozonite" (~100 g) from Wölsendorf, Germany, was used for vacuum mechanical crushing in a MI-1201 time-of-flight mass-spectrometer with a special chamber (V ~ 5 ml).

As the existence time of gases released after a crush is very short (30 seconds; gases are permanently injected), mass spectra in the a.m.u. ranges given below were recorded, full spectra (0-1000 a.m.u.) were not possible yet. Our mass-spectroscopic studies show that the released gas phase consists of $F_2$, $OF_2$, $O_2$, HF, and traces of $H_2O$. The same "antozonite" sample gives off these gases after every single mechanical action up to 100 times in total but the intensity of ion peaks with ***m/e*** values 19, 35, 38 and 54 decreased monotonously after each subsequent mechanical influence. The main gas component was $F_2$, the amount of $OF_2$ was estimated 50-100 times smaller. Heating of the "antozonite" up to 300 °C leads to liberate the gases, resulting in 100 times less intense ion peaks of the previously studied compounds.

To explain the formation and accumulation of molecular fluorine and possibly $OF_2$, two basic geochemical hypotheses have been discussed.

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[1] J. Schmedt auf der Günne, M. Mangstl, F. Kraus, *Angew. Chem.* **2012**, *124*, pp.7968-7971; *Angew. Chem. Int. Ed.* **2012** , *51*, 7847-7849.

## P1.54

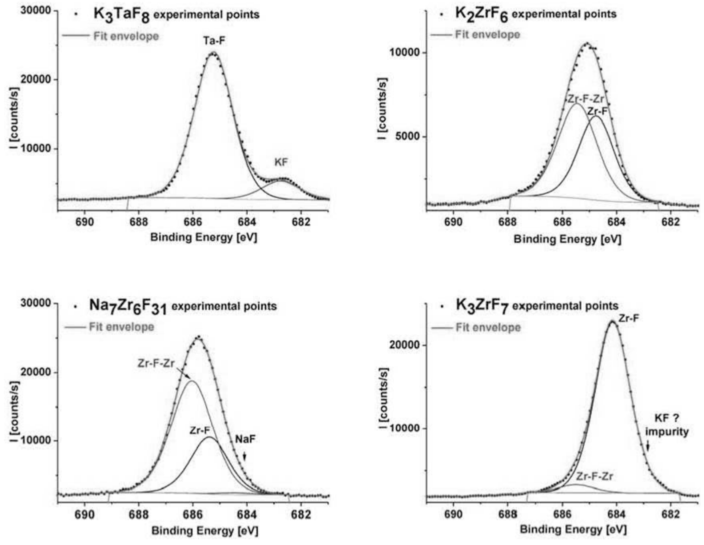
# X-ray Photoelectron Spectroscopy of Inorganic Fluorides

**M. BOCA** [(a)]*

[(a)] INSTITUTE OF INORGANIC CHEMISTRY, SAS, DEPATRMENT OF MOLTEN SALTS - BRATISLAVA (SLOVAKIA)

* miroslav.boca@savba.sk

Molten salt method that is frequently used method for preparation of different materials or pure compound at high temperatures, suffers with one unfavourable but principal complication. When particular phases are mixed and melted some reaction usually takes place and consequent cooling provides product of these chemical or physical processes. The reaction product, however, usually contains impurities that arise either from i) starting components or ii) competitive reactions. Both major and minor phases are either known and fully structurally characterized, or their stoichiometry is believed to be known based on only XRD. The following complications may arise: i) phase characterized by only XRD may happen to be shown as incorrect ii) the unknown phase is present and its composition could be estimated based on isostructural properties, iii) the amount of the phase is below detection limit of XRD and remains unrevealed.



*XPS spectra of investigated compounds*

X-ray photoelectron spectroscopy could reveal the presence of low concentration phases, as unreacted reactants or product of competitive reactions because the detection limit of this spectroscopy is much lower. Moreover, some important information about the structural properties can be retrieved from surface of studied samples.

X-ray photoelectron spectroscopy was applied for identification of differently bonded fluorine atoms in series of compounds NaF, $K_2TaF_7$, $K_3TaF_8$, $K_2ZrF_6$, $Na_7Zr_6F_{31}$ and $K_3ZrF_7$. Three different types of fluorine atoms were described qualitatively and quantitatively. Uncoordinated fluorine atoms (F-) provide signals at lowest binding energies, followed by signals from terminally coordinated fluorine atoms (M—F) and then bridging fluorine atoms (M—F—M) at highest energy. Based on XPS signals assigned to fluorine atoms in compounds with correctly determined structure it was suggested that fluorine atoms in $K_3ZrF_7$ have partially bridging character.

## P1.55

# Crystal Structures of Cesium and Barium Fluorobromates(III)

**S. IVLEV [(a)], P. WOIDY [(b)], F. KRAUS [(b)], V. SHAGALOV [(a)], I. GERIN [(a)], R. OSTVALD [(a)]***

[(a)] Tomsk Polytechnic University - TOMSK (RUSSIA)
[(b)] Technische Universität München, AG Fluorchemie - GARCHING (GERMANY)

* ostvald@tpu.ru

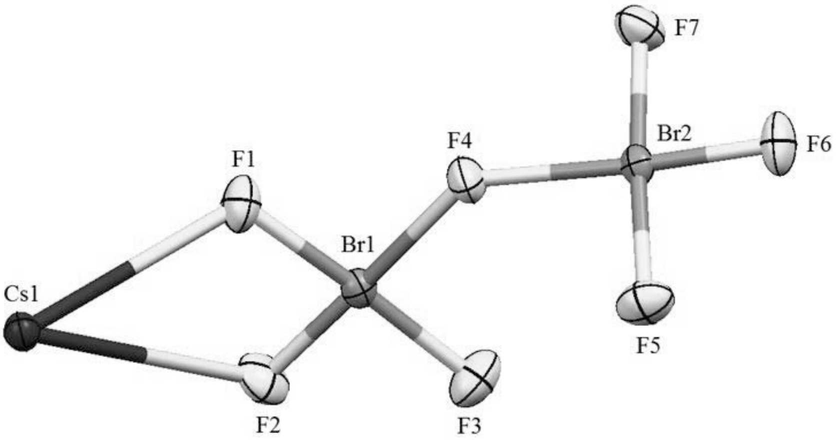


*Fig. 1. Asymmetric unit of $CsBr_2F_7$. Data from single crystal X-ray diffraction, thermal displacement parameters are shown at 70 % at 123 K.*

Fluorobromates(III) of alkali and alkaline-earth metals (the general formula is $Me(BrF_4)_n$) are perspective fluorinating agents in various fields of chemical technology. Despite a noticeable number of research works devoted to this class of chemical compounds, many of their physical and chemical properties are either absent in literature or defined with poor degree of reliance. The main reason for this is extremely high reactivity of all fluorobromates(III), which makes direct measurements of their properties complicated [1].

This problem can be partially solved by using modern *ab initio* methods of solid-state chemistry which allow to estimate the values of some physical and chemical properties of individual compounds with sufficient accuracy. However, the crystal structures, which serve as essential initial data for such calculations, are not determined for all fluorobromates(III) yet. In this study we present our results of crystal structure determination for $CsBrF_4$ and $Ba(BrF_4)_2$ by means of powder X-ray diffraction. Also we succeeded in preparation of single crystals of unusual cesium fluorobromate(III) with one additional molecule of bromine trifluoride $CsBr_2F_7$, which was known before [2], although its crystal structure has been determined for the first time.

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[1] A.A. Opalovskii. Russ. Chem. Rev., October 1967, 711-725.
[2] L. Stein. Complexes of cesium and rubidium fluorides with bromine trifluoride // J. Fluor. Chem., 27 (1985) 249-256.

## P1.56

# Application of *in situ* FTIR Spectroscopy in Hydrofluorination Studies

**E.J. HODGSON** [(a)]*

[(a)] MEXICHEM FLUOR, RESEARCH & TECHNOLOGY - RUNCORN (UNITED KINGDOM)

* emma.hodgson@mexichem.com

Traditionally, laboratory-scale formation of fluoroalkane species through halide exchange using HF, would be monitored by repeated sampling of the hazardous reactor contents, and analysed by methods such as gas chromatography and mass spectrometry. Samples taken in this way are not guaranteed to be representative of the reaction mixture, and may alter the concentration of the remaining composition. The duration of the analytical methods only allows for snap shots of the chemistry to be observed.

An alternative experimental setup has been utilised that addresses all of these issues. An automatic multiple reactor system [1] coupled to an FTIR spectrometer [2], conveniently provides a safe method for monitoring the progression of fluorine chemistry continuously, without the need for regular sampling.

A series of small-scale, highly robust pressure vessels constructed of HF resistant alloys can be used for batch or semi-continuous experiments. The vessels are sited in a compact unit and are heated and stirred independently using the built in solid-state thermostat and mechanical impellers, with real time data logging of pressure, temperature and stirrer speed. Each vessel contains built in FTIR optics, allowing data to be collected *in situ* as frequently as every 30 seconds.

A real-time, continuous log of the reaction progress is available via the profiling of product formation and reactant decay without ever having to extract samples from the mixture (Fig. 1). The process is thus safe and convenient, allows several experiments to be run in parallel, provides representative data of the reaction mixture, and does not alter the concentration of the reaction components.

The FTIR data can be used to generate kinetic information on the main chemistry as well as side reactions such as fouling.

$$\text{R-Cl} \xrightarrow{\text{HF,MX}_4} \text{R-F} + \text{HCl}$$

R = alkyl, vinyl; M = metal, e.g. Ti, Sn; X = halide

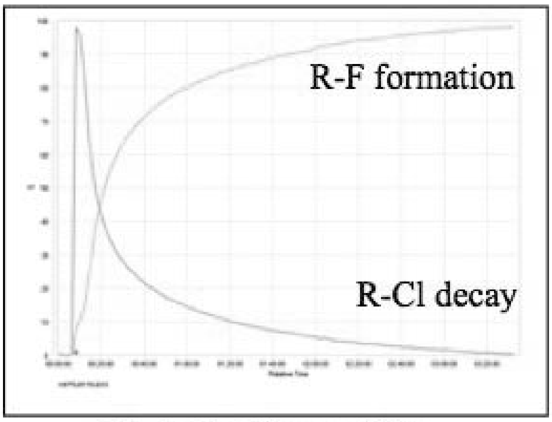

Fig. 1. Reaction profiling.

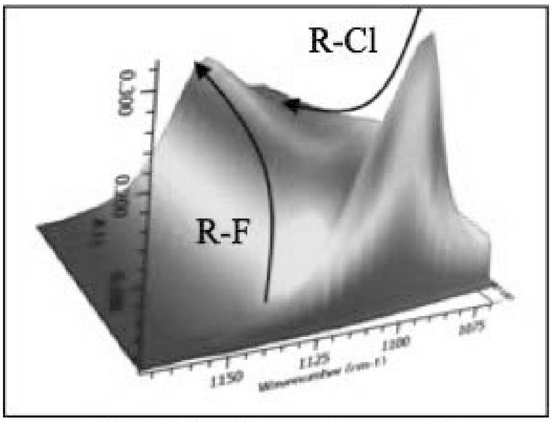

Fig. 2. FTIR spectra over time.

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[1] Mettler Toledo EasyMax™ 102

[2] Mettler Toledo ReactIR™ 45m Fibre Multiplex IR

**P1.57**

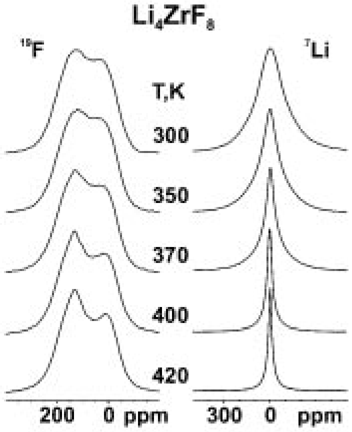
# Ion Mobility in $Li_4ZrF_8$ Compound and $Li_{3.72}Mg_{0.14}ZrF_8$ Solid Solution According to NMR Data

**A. SLOBODUYK** [(a)], **N. DIDENKO** [(a)], **V. KAVUN** [(a)*]

[(a)] Institute of Chemistry, FEB RAS, NMR LAB. - VLADIVOSTOK (RUSSIA)

* kavun@ich.dvo.ru

Among the studied fluorozirconates there are a sufficiently large number of compounds with high ionic conductivity. As a rule, they are cationic conductors containing ammonium, thallium cations [1], although there are fluorozirconates with a mixed anion-cation conductivity – $(NH_4)_2ZrF_6$, $Li(NH_4)_6Zr_4F_{23}$ [2]. The effect of cation substitution in fluorozirconates on anion and cation mobility was studied before, for example, in works [3, 4]. Disordering of the crystal lattice improves ion-conducting properties of the solid solution relative to the stoichiometric compound. Compounds with high conductivity of lithium ions can be used as solid electrolytes in lithium-ion chemical sources of power.



*NMR spectra of the $Li_4ZrF_8$ at different temperature*

This report presents results of NMR studies of ion mobility in $Li_4ZrF_8$ (I) and $Li_{3.72}Mg_{0.14}ZrF_8$ (II) compounds. The shape and width of $^{19}F$ NMR spectra (Fig.) and the time of fluorine spin-lattice relaxation ($T_1$) of compounds I and II in the range of 300–420 K practically does not change. The second moment of $^{19}F$ NMR spectra at 300–420 K is 50 $G^2$, and $T_1$ – 3–5 s. Based on these data, it is possible to assume that there are no motions in the fluoride sublattice of both compounds with a frequency higher than $10^4$ Hz, including reorientations of polyhedra $ZrF_8$ (a rigid lattice, in NMR terms). Transformation of $^7Li$ NMR spectra at temperature increasing 300→420 K (Fig.) corresponds to a dynamically homogenous system and is associated with changing of nature of ion mobility in the lithium sublattice of compounds I and II: rigid lattice → diffusion. The time of spin-lattice relaxation ($T_1$) of the lithium ions depends highly on temperature. Based on relaxation data, the activation energy was determined for diffusion motions of lithium ions: 0.22 and 0.21 ± 0.02 eV for compounds I and II, respectively. Partial substitution of lithium ions by magnesium ions causes an increase of a number of mobile carriers and improves the diffusion characteristics. The invariable activation energy under doping is a natural result, if one assumes that the mechanism of ion mobility in $Li_4ZrF_8$ is based on a vacancy.

The isotropic chemical shifts were defined by $^{19}F$ MAS NMR for magnetically nonequivalent positions of fluorine ions in the structure $Li_4ZrF_8$ that has cavities comparable in size with a size of the polyhedron $ZrF_8^{4-}$. The ratio of a number of potentially mobile cations (lithium) to a number of anions in $Li_4ZrF_8$ is large enough, that is also, in our opinion, one of the conditions necessary for an appearance of ion mobility.

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[1] J. Alizon, J.P. Battut, J. Dupuis et al., *Solid State Commun.*, 47 (1983) 969–972.
[2] V.Ya. Kavun, A.V. Gerasimenko, V.I. Sergienko, et al., *Russ. J. Appl. Chem.*, 75 (2000) 1025–1029.
[3] V.Ya. Kavun, I.A. Tkachenko, N.A. Didenko et al., *Russ. J. Inorg. Chem.*, 55 (2010) 1179–1183.
[4] V. Gaumet, C. Latouche, D. Avignant, J. Dupuis, *Solid State Ionics*, 74 (1994) 29–35

## P1.58

# Phase transitions in defect pyrochlore structure of $CsFe_2F_6$

**M. MOLOKEEV [a], E. BOGDANOV [a], S. MISYUL [b], A. TRESSAUD [c], I. FLEROV [a]***

[a] Kirensky Institute of Physics, SB RAS, CRYSTALPHYSICS LAB - KRASNOYARSK (RUSSIA)
[b] Siberian Federal University - KRASNOYARSK (RUSSIA)
[c] ICMCB-CNRS - PESSAC (FRANCE)

* flerov@iph.krasn.ru

For the first time, structural phase transitions induced by the temperature were found in $A_xM_x^{II}M_{(1-x)}^{III}F_3$ fluorides [1], with the defect pyrochlore structure (*Fd-3m*, Z=8). The detailed XRD patterns have revealed a presence of superlattice reflections in orthorhombic phase of $CsFe_2F_6$ at the room temperature what is in contradiction with the space group *Imma* suggested previously without any certainty for $CsFe_2F_6$ [2]. The symmetry of the Cs compound was determined as *Pnma* (Z=4), as found earlier for related fluorides $NH_4Fe_2F_6$ and $RbFe_2F_6$ [3]. The examination of the temperature stability of orthorhombic structure by differential scanning calorimeter between 100 and 700 K has shown a succession of three phase transitions. The *Pnma* (Z=4)→*Imma* (Z=4)→*I4₁/amd* (Z=4)→*Fd-3m*(Z=8) structural sequence was proposed to occur within a rather narrow temperature range 500 - 560 K. In accordance with group-theoretical analysis the mechanism of structural transformations is mainly associated with the rotation of $(MF_6)$ octahedra (Fig.1) and small displacements of some Fe atoms. That assumption is in good agreement with the low value of the experimental entropy, which is characteristic for displacive transformations.

This study was supported by RFBR (project no. 12-02-00056).

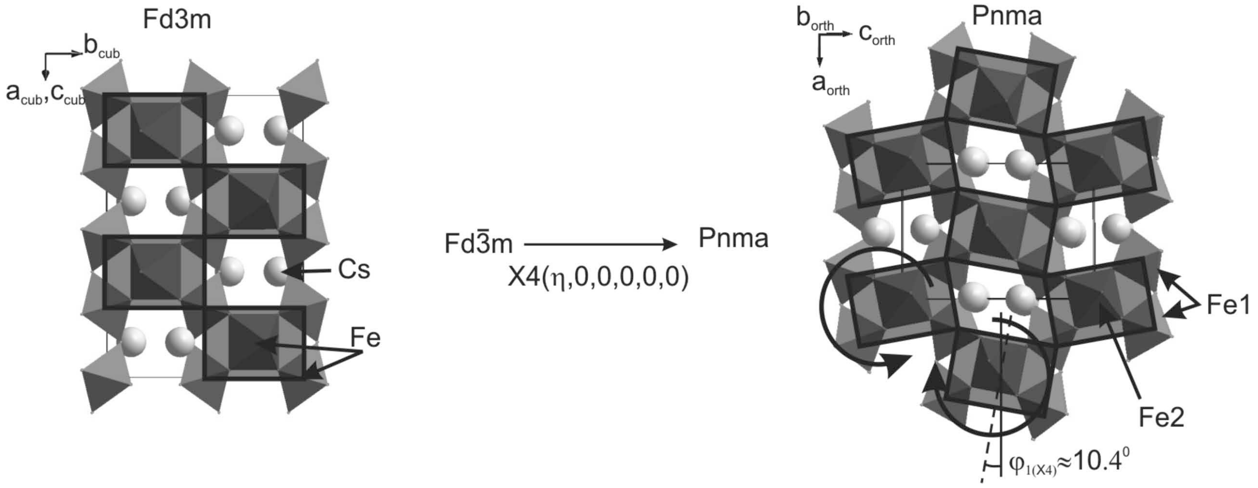

*Fig.1. Transformation mechanism of the cubic phase of CsFe2F6 at 573 K to orthorhombic phase [grey rectangle – cluster of five FeF6 octahedra, arrows show rotation of FeF6].*

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[3] G.Ferey, et.al., *J.Solid State Chem.*, 40 (1981) pp.1-7.

## P1.59

# Fluorine Vacancy Diffusion at Additive Coloring of $CaF_2$ Crystals

**P. FEDOROV** [(a)]*, **A. ANGERVAKS** [(b)], **A. SHCHEULIN** [(b)], **A. RYSKIN** [(b)]

[(a)] A.M. PROKHOROV GENERAL PHYSICS INSTITUTE RUSSIAN ACADEMY OF SCIENCES, LASER MATERIALS AND TECHNOLOGY RESEARCH CENTER - MOSCOW (RUSSIA)
[(b)] National Research University ITMO - ST. PETERSBURG (RUSSIA)

* ppfedorov@yandex.ru

Fluorine diffusion in the process of heating of as-grown pure and doped $CaF_2$ crystals in the reduction atmosphere of Ca vapors (so called “additive coloring (AC)” of the crystals) allows modifying their optical properties. Two opposite processes take place on the surface of the colored crystals: building-up the surface and its decomposition, the former process being prevalent. As a result two flows arise directed from the surface into the bulk: fluorine vacancies and electrons supplied by Ca atoms in vapor phase which participate in building-up the surface.

Under AC of pure crystals recombination of fluorine vacancies with electrons in the crystal bulk results in formation of “simple” (*F*, *M*, *R* and *N*) color centers, which are composed of 1–4 anion vacancies, respectively, with an equal number of electrons [1], “colloidal” centers, two-dimensional metal inclusion embedded into the crystal lattice, which include thousands of anion vacancies/electrons, and quasi-colloidal centers of unknown structure; it is likely that they are in an intermediate position between simple and colloidal center by the number of these components. All centers have characteristic absorption bands. Under the impact of radiation resonant to one or another band and the temperature the center conversion occurs. $CaF_2$ with color centers is used as highly-stable volume holographic media [2].

Under AC of crystals doped with rare-earth (RE) ions (laser media) vacancies recombine first of all with interstitial $F^-$ ions that compensate +1 extra change of $RE^{3+}$ ions in as-grown crystal whereas electrons realize $RE^{3+}$®$RE^{2+}$ conversion. Three features of coloring these crystals are as follows: (1) sharp slowing-down the coloring process, (2) larger concentration of vacancies/electrons that can be introduced in the crystal and (3) sharper border between colored and non-colored segments of the crystal [3].

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## P1.60

# Synthesis and Reactivity of Rhodium(I) Silyl and Germyl Complexes

**T. AHRENS** [(a)*], **A.L. RAZA** [(a)], **M. TELTEWSKOI** [(a)], **T. BRAUN** [(a)]

[(a)] Humboldt-Universität zu Berlin, Department of Chemistry - BERLIN (GERMANY)

* ahrensth@cms.hu-berlin.de

One way to access fluorinated building blocks consists of a selective C–F bond cleavage of highly fluorinated or perfluorinated molecules. The activation of C–F bonds mediated by transition metals complexes are meanwhile fairly well established [1]. The thermodynamic driving force for C–F bond activation reactions is usually the formation of another strong bond like a H–F, Si–F, B–F or even a M–F bond. However, subsequent derivatization reactions of the fluorinated molecules after the C–F bond cleavage step are rare.

The synthesis and reactivity studies of the highly reactive rhodium boryl complex [Rh(Bpin)$(PEt_3)_3$] and silyl complexes like [Rh{Si$(OR)_3$}$(PEt_3)_3$] (R = Me, Et) revealed an extraordinary reaction pattern towards fluorinated compounds [2]. For example, the activation of pentafluoropyridine affords selectively the C–F activation product [Rh(2-$C_5NF_4$)$(PEt_3)_3$]. A Selective activation at the 2-position is difficult to achieve, but in these cases preferred. An analogous behavior was observed for the rhodium germyl complex [Rh($GePh_3$ )$(PEt_3)_3$]. We will report on the synthesis and properties of rhodium silyl and germyl complexes towards C–F bond activation reactions.

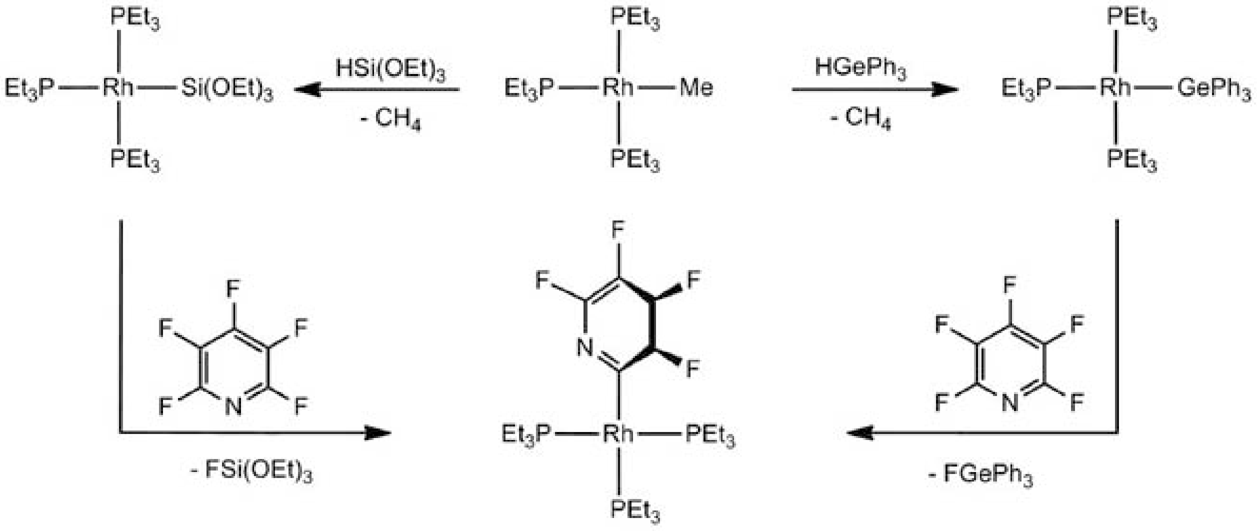

*Fig. 1. Synthesis of rhodium(I) silyl and germyl complexes and their reactivity in C–F bond activation reaction with pentafluoropyridine.*

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## P1.61

# Synthesis of nickel- and palladium fluorido complexes: Applications in catalytic cross-coupling reactions

**J. BERGER** [(b)]*, **T. BRAUN** [(b)]

[(b)] Humboldt-Universität zu Berlin, Department of Chemistry, DEPARTMENT OF CHEMISTRY - BERLIN (GERMANY)

* bergerjo@student.hu-berlin.de

Fluorinated entities are versatile building blocks in pharmaceuticals, agrochemicals and advanced materials.[1] One possible pathway to synthesize fluorinated molecules is the transition metal mediated derivatization of highly fluorinated precursors. The conversion can involve a C-F activation step to access a fluorinated building block. Several examples for catalytic cross-coupling reactions at palladium or nickel are described in the literature. It was also discussed whether a hemilabile coordinating ligand has a beneficial effect on the efficiency of the cross-coupling reactions.[3]

We recently reported on the formation of the nickel(II) fluorido phosphine complexes by C-F activation of pentafluoropyridine at $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) in the presence of the hemilabile coordinating ligands $^iPr_2PCH_2CH_2OMe$ or $^iPr_2PCH_2CH_2NMe_2$.[4] In the case of $^iPr_2PCH_2CH_2NMe_2$ the amino group coordinates to the metal center resulting in the formation of the monophosphine complexes $[Ni(F)(2\text{-}C_5NF_4)(\kappa^2\text{-}(P,N)\text{-}{}^iPr_2PCH_2CH_2NMe_2)]$ (1) and $[Ni(F)(4\text{-}C_5NF_4)(\kappa^2\text{-}(P,N)\text{-}{}^iPr_2PCH_2CH_2NMe_2)]$ (2) (see figure 1). The complexes 1 and 2 (ratio 1:2) are able to catalyze the conversion of pentafluoropyridine to 3,5-difluoro-2,4,6-triphenylpyridine in the presence of $PhB(OH)_2$.

Another possibility to build up fluorinated molecules is the transition metal mediated fluorination of non-fluorinated molecules with the help of either electrophilic or nucleophilic fluorinating agents.[5] To gain more detailed insights into the mechanistic pathways the reaction of palladium and nickel complexes bearing the hemilabile coordinating ligand $^iPr_2PCH_2CH_2NMe_2$ towards NFSI were investigated. Further studies focused on the reactivity of the resulting fluoro complexes towards various organic substrates.

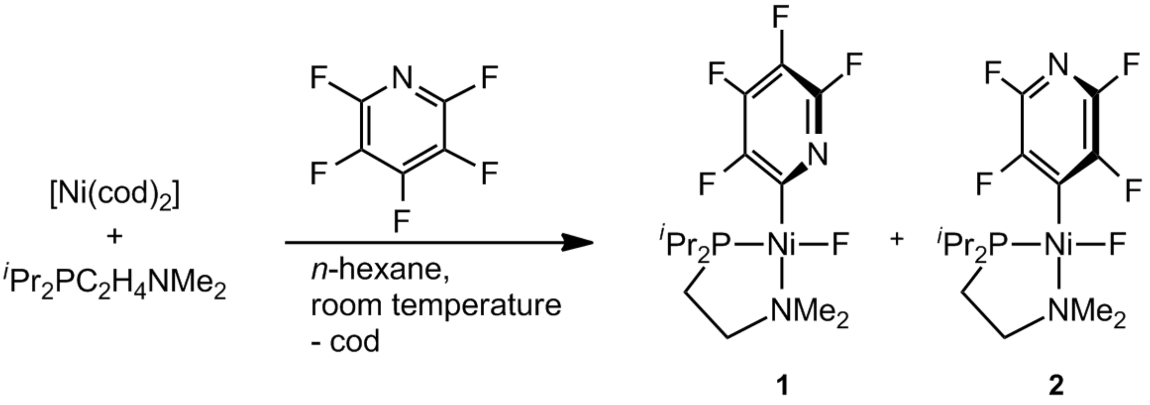

*Fig. 1. Formation of nickel-fluorido complexes.*

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## P1.62

# Synthesis and Properties of Calcium Fluoride Sol

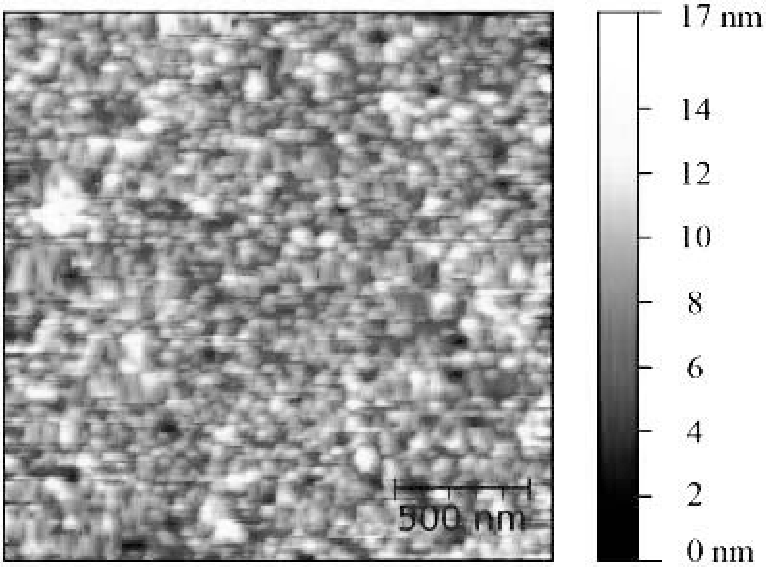
**A. REHMER** [(a)], **E. KEMNITZ** [(a)]*

[(a)] Humboldt-Universität zu Berlin, DEPARTMENT OF CHEMISTRY - BERLIN (GERMANY)

* erhard.kemnitz@chemie.hu-berlin.de

A method for the preparation of *nanosized* calcium fluoride sols was developed using calcium acetate monohydrate ($Ca(OAc)_2 \times H_2O$) as calcium precursor, ethanol/acetic acid as solvent and ethanolic hydrogen fluoride solution. This method based on the fluorolytic sol-gel synthesis which was developed recently for HS-$AlF_3$[1] and $MgF_2$[2].

Calcium fluoride exhibts a low refractive index of 1.43 and shows high transparency over a wide range from infrared (IR) up to the vacuum UV (130 nm) making it a material of interest for optics, such as in anti-reflecting coating and wavelength filters.



*AFM topography of calcium fluoride on glass*

The clear sols obtained this way, are stable over weeks and contain homodispersed *nanosized* particles with a diameter of approximately 2 nm. These $CaF_2$-sols can be used for dip- or spin-coating applications on glass or Si-wafer.

Figure 1 displays an antireflective (AR) $CaF_2$-layer on glass which was measured by atomic force microscopy (AFM). The calculated average surface roughness of a $CaF_2$-layer is about 1.55 nm and the average height is about 17 nm. For $MgF_2$-layers a calculated average surface roughness of about 2.77 nm and an average height of about 30 nm was found. Thus, $CaF_2$-layers exhibits better topological properties than $MgF_2$-layers.

The refractive index of such $CaF_2$-layers varies between 1.20 and 1.36 depending on the concentration and solvent of the $CaF_2$-sols.

In sum, a method has been developed which provides the access to clear transparent $CaF_2$-sols that are suitable for the preparation of antireflection-layers with good optical properties. Optical and chemical data of such $CaF_2$-AR-layers will be presented.

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## P1.63

# Synthesis and study of bismuth containing oxyfluoroniobate glasses

**N. SAVCHENKO** [(a)]*, **L. IGNATEVA** [(a)], **T. ANTOKHINA** [(a)], **S. POLYSHCHUK** [(a)], **Y. MARCHENKO** [(a)], **V. BOUZNIK** [(b)]

[(a)] INSTITUTE OF CHEMISTRY FEB RAS, LABORATORY OF FLUORIDE MATERIALS - VLADIVOSTOK (RUSSIA)
[(b)] BAIKOV INSTITUTE OF METALLURGY AND MATERIALS SCIENCE RAS - MOSCOW (RUSSIA)

* savchenko@ich.dvo.ru

We obtained new glasses in the systems $MnNbOF_5$-$BaF_2(PbF_2)$-$BiF_3$ and $NbO_2F$-$BaF_2$-$ZnF_2$-$BiF_3$, which are characterized by a wide glass-forming range. Samples were studied by the XRD, IR and Raman spectroscopy, differential scanning calorimetry (DSC) and impedance spectroscopy. It was shown by IR and Raman spectroscopy that the glass structures are formed from $Nb(OF)_6$ polyhedra connected in networks by fluorine or oxygen bridges. And IR- both Raman spectra showed the existence of the band in the region 300 $cm^{-1}$ characterizing Bi-F vibrations confirming the presence of $BiF_n$-polyhedra in the glass networks. $BiF_3$-polyhedra form its own lays or spheres. Thermal treatment of the glasses obtained was carried out to the bitter end of crystallization. The samples obtained in the process of treatment at suitable temperatures were analyzed. Raman spectra for the glasses showed that the crystallization of some of the samples passes though the stages of liquation. At the defined temperatures we successfully obtained the transparent glassceramics havig the crystalline phase of the composition $Ba_{1-x}Bi_xF_{2+x}$ in the glass matrix. The data on electrical conductivity of individual solid solutions with fluorite-type structure of the same composition were described in [1]. So, on the base Bi-containing glasses we can obtain glassceramics having in the glass matrix the crystallites with important physical properties. We investigated the conductivity of new oxyfluoride glasses in the system $20MnNbOF_5$-$xBaF_2$-$yBiF_3$, identified the nature of conduction, and determined the dependence of the conductivity on the glass composition. The electrical conductivity is the highest in the glasses $20MnNbOF_5$-$30BaF_2$-$50BiF_3$ and $20MnNbOF_5$-$40BaF_2$ -$40BiF_3$ ($\sigma = 7.46 \times 10^{-3}$ S/cm at 533 K and $\sigma = 1.78 \times 10^{-3}$ S/cm at 523 K, respectively); i.e., in the glasses with the highest $BiF_3$ content. The features of electrophysical properties of glasses in the studied system can be explained by their structural features, which were previously identified by IR and Raman spectroscopy [2, 3].

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## P1.64

# X-Ray Structure and Spectroscopic Investigation of Phosphoryl Fluoride

**M. FELLER** [(a)]*, **K. LUX** [(a)], **A. KORNATH** [(a)]

[(a)] LUDWIG-MAXIMILIAN UNIVERSITY, DEPT. OF CHEMISTRY - MUNICH (GERMANY)

* michael.feller@cup.uni-muenchen.de

The crystal structure of phosphoryl fluoride was determined by single-crystal X-ray diffraction. Due to the low melting point of $POF_3$, the crystal was grown in a capillary directly in the cooling stream of a X-ray diffractometer. Phosphoryl fluoride crystallizes in the space group *P*-3m1 with two molecules in the unit cell. The results of the X-ray structural analysis of solid $POF_3$ were compared with the gas phase structure and the structure of the $POF_3 \cdot 2SbF_5$ adduct. The spectroscopic characterization of $POF_3$ was performed in all three aggregate states. In addition to the experimental results quantum chemical calculations are discussed.

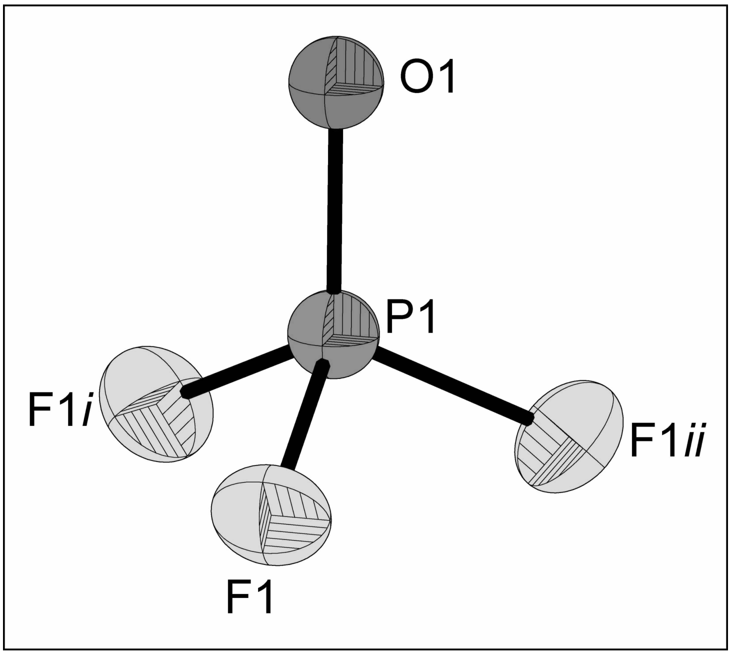

*Fig. 1: Molecular structure of POF3 showing the 50% probability displacement ellipsoids. [Symmetry code: i = 1-y, x-y, z; ii = 1-x+y, 1-x, z]*

**P1.65**

# Synthesis and characterization of vanadium (V) oxyfluoride, $VOF_3$

**R. BENZOUAA [a]*, A. HAMWI [b], M. DUBOIS [b], D. AVIGNANT [b], E. PETIT [b], A. SELMI [c], B. MOREL [c]***

[a] Institut de Chimie de Clermont-Ferrand, Equipe Matériaux Inorganiques - AUBIERE CEDEX (FRANCE)
[b] Institut de Chimie de Clermont-Ferrand - AUBIERE CEDEX (FRANCE)
[c] AREVA/COMURHEX - PIERRELATTE (FRANCE)

* bertrand.morel@areva.com

Only few informations are available, in the literature about the synthesis and the physico-chemical characterization of vanadium (V) oxyfluoride $VOF_3$. Due to potential applications in several fields such as: phosphoryl enzymes transfer where the vanadate can generate a trigonal-bipyramidal coordination on the active site [1], or in electrochemical systems where the intercalation of vanadium oxyfluoride into graphite results in high mixed electronic and ionic conduction materials for lithium ions batteries[2]. The synthesis of this oxyfluoride has been reinvestigated in order to proceed to the determination of its physic-chemical properties.

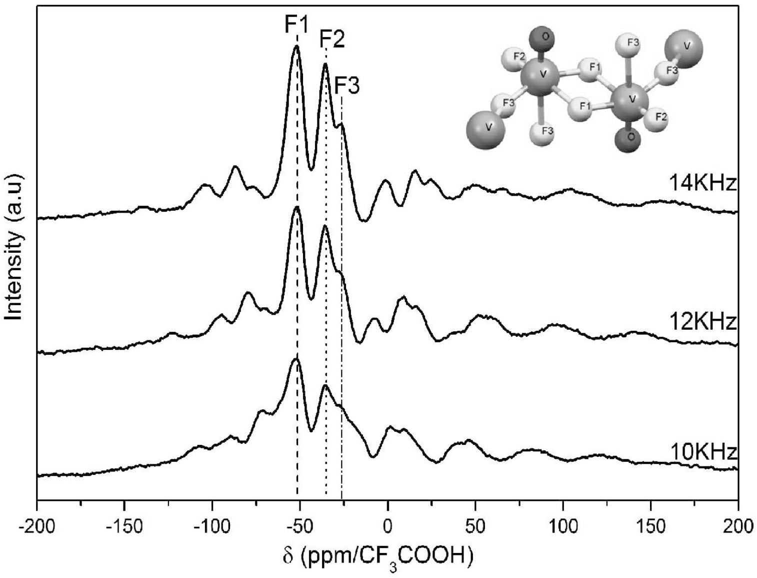

*Fig. 1: 19F MAS NMR spectra of the as-prepared VOF3 recorded at 10, 12 and 14 KHz*

This work deals with an original one-step synthesis of high purity $VOF_3$, without further post-sublimation. Fluorination and condensation of the gaseous phase were simultaneously carried out. The physico-chemical characterizations were investigated by Infrared spectroscopy, Raman diffusion and high resolution solid state $^{19}F$ NMR. Its vapor pressure was determined in the 20 -70°C temperature range.

The structure of $VOF_3$ has initially been solved by Supel et al. [3] from single crystal data. The $^{19}F$ NMR data are interpreted on the basis of the structural description (Fig. 1),i.e. one vanadium, three fluorine and one oxygen sites, all of them in general Wyckoff position.

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## P1.66

# Synthesis of New Fluorinated Building Blocks for Statin Analogues

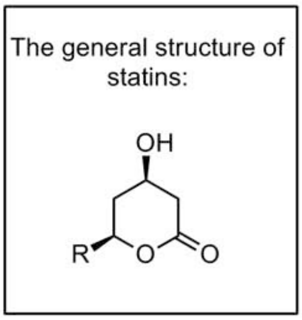
**H. BERLEMANN** [(a)]*, **I. KONDRATOV** [(b)], **G. HAUFE** [(a)]

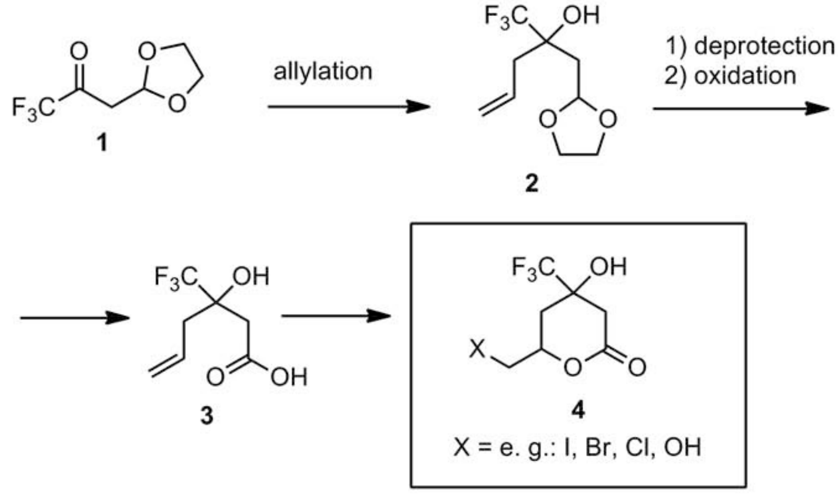
[(a)] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)
[(b)] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)

* berleman@uni-muenster.de

Statins belong to an important class of drugs for the treatment of hypercholesterolemia due to their ability to inhibit the 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase. Fluvastatin, Atorvastatin, Rosuvastatin and Pitavastatin are the most well-known compounds from the family. The main structural feature of statins is the presence of the 3-hydroxy-valerolactone moiety playing the crucial role in binding [1]. While a lot of statins and their analogues (including some fluorine containing compounds) were widely investigated, little attention was paid to analogues which contain fluorine in the lactone fragment [2], although the introduction of fluorine or fluorine-containing substituents into the lactone moiety can change or even improve this activity. In this case fluorinated building blocks, which can be used for the preparation of corresponding statin analogues are of interest.

Here we present the synthesis of hitherto unknown building blocks 4, containing a trifluoromethyl group in 3-position of the lactone ring. The synthesis starts from ketoacetal 1 which was earlier described [3]. The allylation, deprotection of the aldehyde group and it's oxidation to the acid lead to the acid 3 which can be transformed to the lactones 4 by halolactonization reactions. Compounds 4 are useful building blocks for the synthesis of new statin analogues bearing a trifluoromethyl group in the lactone ring.





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## P1.67

# Hydrolyzed Fluorocarbon Nanocomposition Materials and Their Applications in Sorption and Biomedical Technologies

**L. LEVCHENKO** [(a)]*, **V. MITKIN** [(a)]

[(a)] NIKOLAEV INSTITUTE OF INORGANIC CHEMISTRY SB RAS - NOVOSIBIRSK (RUSSIA)

* llm17@ngs.ru

A new class of the hydrolyzed nanocomposite fluorocarbon materials (FCM-OH) and their use as highly porous novel functional multiphase systems for sorption technologies is considered. The main requirement for these new FCM-OH was the necessity to achieve good hydrophilic properties, whereas starting FCMs, are known to exhibit high hydrophobicity [1].

By means of hydrolysis of a nanosized mesoporous superstoichiometric fluorocarbon material FS ($CF_{1.20\pm0.03}$) and carbon-fluorocarbon nanocomposites NCFC ($CF_{0.93\pm0.03}$)by 10% KOH in aqueous-alcoholic solution two new classes of the hydrolyzed fluorocarbon nanomaterials were obtained: hydroxy-fluorocarbon nano-material FS-OH ($sp^3$-$C_{1-y}F_{n-x}(OH)_x$, where $n=1$; $x>0.1$, $y\sim0.05$-$0.1$) and carbon-hydroxy-fluorocarbon nanocomposites NCFC-OH of general formula $sp^2$-$C_{m*}sp^3$-$C_{1-y}F_{n-x}(OH)_x$, where $n = 1$; $x \sim 0$; $y \sim0.1$-$0.2$ [2].

XRD, FTIR data and C,H,F-analyses for FS-OH and NCFC-OH products have allowed to state that hydrolysis of FS and NCFC in KOH solutions can be explained by the substitution reactions of surface $sp^3$-C-F-groups by $sp^3$-C-OH-groups. The blocks forming FS-OH and NCFC-OH nanocomposite materials are built of nanoglobules of fluorocarbon matrices $sp^3$-C-F with a layered network, which surface is covered by layers of hydroxygraphenes $sp^3$-C (OH), and edges of $sp^3$-C-F-nets containing a considerable quantity of functional groups $sp^2$ >C=O and $sp^2$ >COOH. The distinctive feature of new FS-OH and NCFC-OH matrices is a combination of excellent hydrophilic and hydrophobic properties at the nano-scale within their internal nanopores.

On the basis of new FS-OH and NCFC-OH matrices there new sorption highly porous nanomaterials - FS-OH-X and NCFC-OH-X, where X = $Cl_2$, $I_2$, $N(C_8H_{17})_3$, $C_6H_5NH(C_8H_{17})$, $CaS_2$, were prepared and exhibited excellent properties of solid extractants (Sol-Ex).

The perspectives of R&D are the creation of new sorbents for modern and future industrial technologies for alkali and $Cl_2$ production, demercurisation of industrial wastes, production of high-purity lithium salts, extraction of toxicants, purification of water and also for recovery of radionuclides Cs, Sr, etc. from liquid radioactive water and organic wastes and of biomedical applications, as improved hemo- and enterosorbents and matrices for drug delivery in biomedical researches.

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## P1.68

# Technology of high-purity silicon dioxide production

**A. DYACHENKO [a]*, R. KRAYDENKO [b], A. KISELEV [b]**

[a] Tomsk Polytechnic University, Department of Rare, Scattered and Radioactive Element Technology - TOMSK (RUSSIAN FEDERATION)
[b] Tomsk Polytechnic University - TOMSK (RUSSIAN FEDERATION)

* atom@tpu.ru

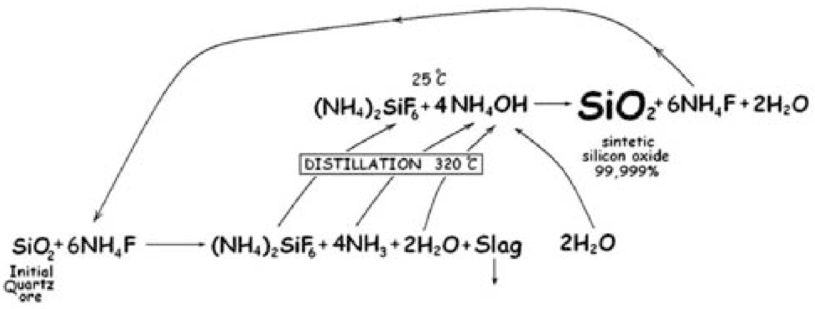


*Fig. 1. – Schematic diagram of ammonium fluoride treatment of silicon dioxide*

Production of high-purity silica-5N ($SiO_2$ content over 99.999%) is an important and urgent task of the modern chemical industry. This material is used in the manufacture of optical glass, optical fibers for internet cables, silicon for solar power and electronics.

The existing technologies of synthetic silicon dioxide were introduced in the mid-twentieth century. These methods are energy-consuming, multi-step and do not meet stringent environmental requirements. In fact, as some conventional technologies became obsolete; it became necessary to develop new methods for the production of synthetic silica. We believe that the fluoride technology of processing of quartz materials by ammonium fluoride is the most promising direction.

Implementation of a new method for producing high-purity silica is carried out in the Tomsk Polytechnic University. Fluoride technology is used as the basis of the method. Ammonium fluoride is selected as a fluorinating reagent, which is a waste byproduct of fluoride industries such as aluminum and plastics plants. The molten ammonium fluoride is a strong fluorinating reagent. The advantages of $NH_4F$ are vigorous interaction with the molten silicon oxide, and forming a solid $(NH_4)_2SiF_6$.

$$SiO_2 + 6NH_4F = (NH_4)_2SiF_6 + 2H_2O + 4NH_3$$

Upon heating, $(NH_4)_2SiF_6$ sublimes without decomposition, and desublimes when cooled - this property is used to clean impurities from the quartz concentrate. Purified $(NH_4)_2SiF_6$ treated with ammonia water which accompanies with regeneration of the fluorinating agent.

$$(NH_4)_2SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O$$

Then the hydrated silica is separated by the filtration from the solution of ammonium fluoride. The separated solution of ammonium fluoride is evaporated and crystallized in the form of technical ammonium fluoride with composition of 25% $NH_4F$, 75% $NH_4F \cdot HF$. Silicon dioxide in finely divided form is obtained by drying and calcining of the precipitate.

Experiments of silicon dioxide production were carried out at pilot equipment designed at Tomsk Polytechnic University. The research results allows to start the pilot production of high-purity synthetic silicon dioxide with the content of the base material $SiO_2$- 99,999%.

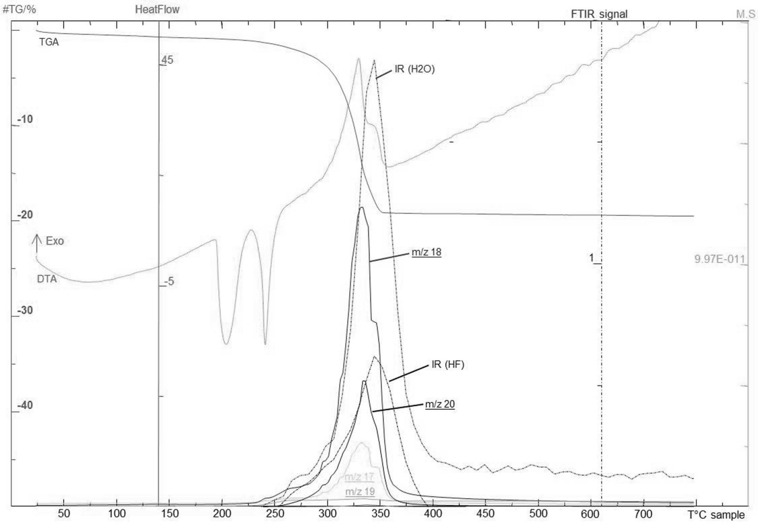
## P1.69

# In-situ determination of $F_2$ direct fluorination mechanisms of metal fluorides by TGA measurements

**E. DURAND** [a]*, **B. GUILLAUME** [a], **C. PEPIN** [a], **A. TRESSAUD** [a], **A. DEMOURGUES** [a]

[a] ICMCB-CNRS - PESSAC (FRANCE)

* edurand@icmcb-bordeaux.cnrs.fr



$F_2$-gas is one of the most powerful oxidizing agents to get high oxidation states in metal fluorides. The Bordeaux Fluorine group was deeply involved since the sixties on the synthesis of these high oxidation states using elemental fluorine[1]. Then, high valency metal fluorides can also release elemental fluorine after thermal treatment under inert gas or vacuum. For instance, rare earth such as $Ce^{IV}$ in $CeF_4$, or transition metals such as $Co^{III}$ in $CoF_3$ /$KCoF_4$ or $Ni^{IV}$ in $K_2NiF_6$ can be used as fluorinating agents [2]. The $F_2$-uptake of $CeF_3$, $CoF_2$, $KCoF_3$ or $K_2NiF_4$ under 10%$F_2$/Ar gas mixture can be followed up to T=500°C by thermogravimetric analysis (TGA) measurements and various thermal phenomena can be observed. Conversely, the release of fluorinated species such as HF, $MF_x$, $CF_x$ can be identified after thermal treatment under inert gas using TGA coupled simultaneously with mass spectrometer (MS) and Fourier transform infrared spectroscopy (FTIR). One should have to notice that the detection of evolving elemental fluorine is decisive but awkward in such conditions, because of its extreme reactivity. This original experimental set-up (based on Setaram Setsys technologies) is therefore able to bring valuable information on the *in-situ* reactivity of numerous old and new inorganic fluorides[3] under elemental fluorine or anhydrous HF.

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## P1.70

# Synthesis of multifunctional β-$NaYF_4$:Yb:Er@$NaYF_4$ @ $(TBA)_2$ $Mo_6Br_8F_6$@$SiO_2$ core-shell nanoparticles: Radiative excitation of luminescence cluster from upconversion nanoparticles

**D. THANGARAJU** [(a)*], **P. GREDIN** [(b)], **M. MORTIER** [(c)], **T. AUBERT** [(d)], **C. NEAIME** [(d)], **S. CORDIER** [(d)], **F. GRASSET** [(d)]

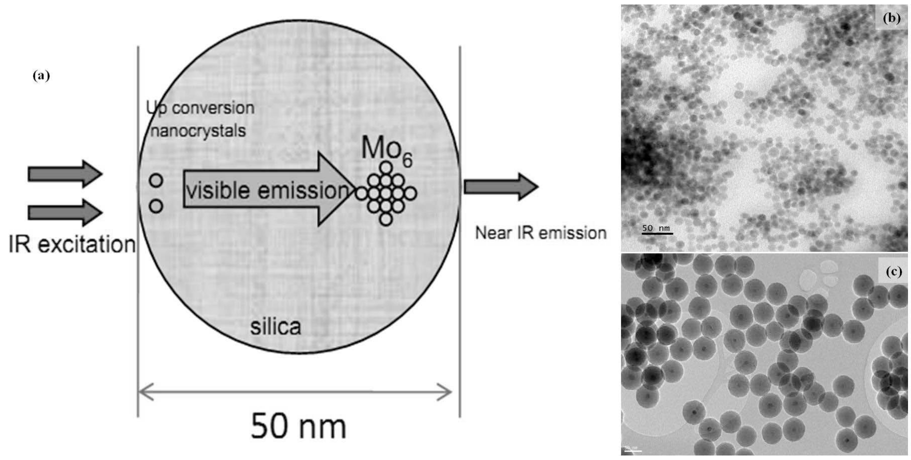
[(a)] LMCP, LABORATOIRE DE CHIMIE DE LA MATIÈRE CONDENSÉE - UMR 7574 -CAES - PARIS (FRANCE)
[(b)] LMCP, Ecole Nationale Supérieure de Chimie de Paris - Site Curie - PARIS (FRANCE)
[(c)] ENSCP, LCMCP - PARIS (FRANCE)
[(d)] UMR-CNRS 6226, Institut des Sciences Chimiques de Rennes, Groupe Chimie du Solide et Matériaux,, Université de Rennes 1 - RENNES CEDEX (FRANCE)

* d-thangaraju@etu.chimie-paristech.fr

Multifunctional composite up-converting rare-earth nanophosphors (UCNPs) have attained considerable interest in the biological applications.[1] The goal of this work is to realize the nanodevices built up from β-$NaYF_4$:Yb:Er@$NaYF_4$ nanoparticles and $(TBA)_2Mo_6Br_8F_6$ cluster compounds embedded inside silica nanoparticles. In these devices, the upconversion (UC) fluoride nanoparticles absorb infrared wavelengths and emit visible radiation exciting efficiently at the same time the $Mo_6$ clusters which then produce infrared emission (Fig. 1(a)).

Monodisperse colloidal UC β-$NaYF_4$:Yb:Er nanoparticles have been synthesized by co-thermolysis of alkali and rare-earth trifluoroacetates in oleylamine at 330°C. Subsequent undoped epitaxial layer was prepared by the precursor hot-injection method to enhance its upconversion emission. The hexagonal structure of the derived UC particles was verified with powder XRD patterns and a spherical morphology with monodispersed size (12 nm) was observed in TEM measurements (Fig. 1. (b)). UC luminescence spectra of β-$NaYF_4$:Yb:Er colloidal nanoparticles indicate that the derived particles exhibit excellent green/red emission under 980 nm excitation and enhanced UC emission of β-$NaYF_4$:Yb:Er@$NaYF_4$ was proved with higher UC emission intensity.[2] Monodispersed β-$NaYF_4$:Yb:Er@$SiO_2$ core-shell nanoparticles were synthesized in heptane medium using TEOS and TEM micrographs of these particles show that amorphous silica layer surrounded individual β-$NaYF_4$:Yb:Er nanoparticles (Fig. 1. (c)).

β-$NaYF_4$:Yb:Er@$NaYF_4$@$(TBA)_2Mo_6Br_8F_6$@$SiO_2$ nanoparticles will be synthesized by microemulsion process. These multifunctional nanoparticles should exhibit visible and/or red-NIR luminescence under NIR excitation and/or visible excitation.



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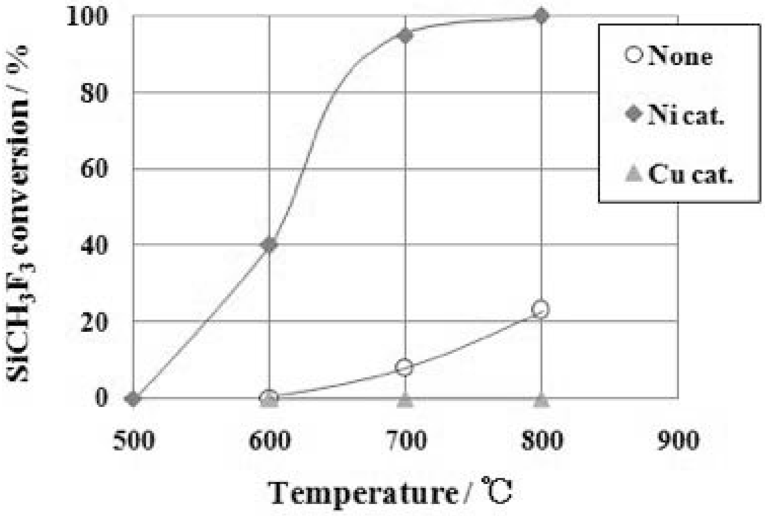
P1.71

# Production process for high-pure silicon tetrafluoride by silicon and hydrogen fluoride

**T. SHIBAYAMA** [(a)]*, **A. RYOUKAWA** [(a)], **H. ITOH** [(a)], **R. NAKAMURA** [(a)], **S. NAKAGAWA** [(a)]
[(a)] CENTRAL GLASS CO., LTD., CHEMICAL RESEARCH CENTER(UBE) - UBE CITY (JAPAN)
* takaaki.shibayama@cgco.co.jp

An industrial production process of high-pure $SiF_4$, the ingredient of semiconductor's insulating layer or optical fiber, was developed. Although reaction of Si and $F_2$ or reaction of $SiO_2$ and HF in sulfuric acid were known as conventional processes, in this study, low cost and supply stable ingredients, industrial grade Si (98% purity) and industrial grade HF (99.9% purity), were employed.



*Correlation of catalyst and $SiCH_3F_3$ conversion (Ni tubular reactor[φ25mm,700mm], Space velocity = 3.2cm/s, Catalyst[None, Ni mesh, Cu mesh])*

$$Si + 2F_2 \rightarrow SiF_4 \quad \Delta G_f^0 = -1573.6 \text{ kJ/mol}$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \quad \Delta G_f^0 = -72.7 \text{ kJ/mol}$$
$$Si + 4HF \rightarrow SiF_4 + 2H_2 \quad \Delta G_f^0 = -472.0 \text{ kJ/mol}$$

Si was filled in a tubular reactor and HF was circulated into it. Reaction of Si and HF promptly proceeded above 400°C. Here, reactivity of HF was more than 99.99%, selectivity of $SiF_4$ was 96% and $SiHF_3$ was detected as a fluorosilane by-product. In case Si did not exist, $SiHF_3$ reacted easily with HF to $SiF_4$. Moreover, carbon-containing compounds like $CH_4$ and $SiCH_3F_3$ were generated because industrial grade Si includes carbonous impurities. $SiCH_3F_3$ was converted into $SiF_4$ by HF with Ni catalyst (Fig.1).

$$SiHF_3 + HF \rightarrow SiF_4\ H_2 \quad \Delta G_f^0 = -130.5 \text{ kJ/mol}$$
$$SiCH_3F_3 + HF \rightarrow SiF_4 + CH_4 \quad \Delta G_f^0 = -178.9 \text{ kJ/mol}$$

## P1.72

# Iodine Transfer Polymerization (ITP) of trifluoroethylene

**A. ALAAEDDINE** [(a)], **Y.R. PATIL** [(a)], **V. LADMIRAL** [(a)*], **B. AMEDURI** [(a)]
[(a)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)
* vincent.ladmiral@enscm.fr

Fluoropolymers are a very interesting class of polymers with remarkable properties, such as thermal stability, chemical inertness (to acids, bases, organic solvents), low refractive indices and dielectric constants. They also are hydrophobic and lipophobic, display excellent weather resistance and can be elastomer or thermoplastic. These high- added-value materials have thus found applications in numerous high technology fields such as aeronautics, microelectronics, optics, textile finishing, nuclear industry, paints and coatings, photovoltaic devices, and lithography.

Polytrifluoroethylene (PTrFE) is a very interesting example of fluoropolymer as it exhibits along with poly(vinylidene fluoride) (PVDF) pyro-, piezo-electricity, and also ferro-electric properties.

These specialty polymers are usually produced by radical (co)polymerization of fluorinated monomers. Iodine Transfer Polymerization (ITP) is a controlled radical polymerization technique based on degenerative transfer between polymer radicals and iodine-capped polymer chains. ITP is particularly well-suited to the polymerisation of fluorinated olefins such as VDF and TrFE; and has been successfully used to prepare well defined PVDF-based polymeric architectures. This work describes the first ever ITP of TrFE. The preparation and characterization (Figure 1) of well-defined PTrFE homopolymers and PTrFE-containing block copolymers will be presented in details.

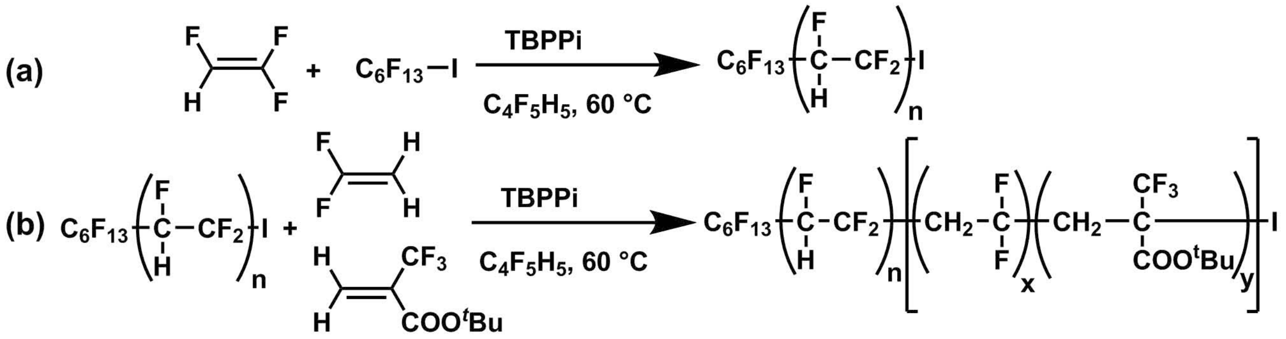


*Figure 1. (a) ITP of TrFE, and (b) chain extension of PTrFE by Iodine transfer copolymerisation of VDF and tert-butyl 2-trifluoromethacrylate. TBPPI stands for tert-butyl peroxypivalate.*

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## P1.73

# Synthesis, copolymerization and polymer properties of 2-Trifluoro-methacrylic acid ester of a fluorinated alcohol

**M.N. WADEKAR** [(a)]*, **Y.R. PATIL** [(a)], **B. AMEDURI** [(a)]

[(a)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)

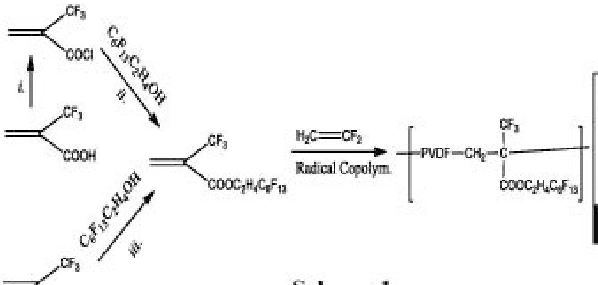
* Wadekar.Mohan@enscm.fr

Due to the exceptional properties of the self-cleaning materials, antifouling surfaces, and stain resistant textiles, highly hydrophobic materials have attracted a great attention since the recent decades.

Novel hydrophobic polymers were obtained by free radical copolymerization (FRP) of an original monomer based on 2-trifluoromethyl acrylic acid ester of fluorinated alcohol (MAF-$R_F$) with vinylidene fluoride (VDF). MAF-$R_F$ has been synthesized in good to very good yields via two different synthetic routes (Scheme 1). 1) By trans-esterification reaction of ter-butyl α-trifluoromethacrylate using 97% sulfuric acid with a fluorinated alcohol and 2) By esterification of 2-trifluoromethacryloyl chloride with the alcohol.

Conventional FRP of MAF-$R_F$ with VDF in solution provide copolymers with interesting polymer properties. MAF-$R_F$, like other MAF esters [1,2] does not homopolymerize but is more reactive than VDF in radical polymerizations and forms almost alternating copolymers above ca. 12 mol% of MAF-$R_F$ in the feed. Water contact angle study (Figure 1) clearly suggests that the hydrophobicity of these copolymers improve with increasing percentage of MAF-$R_F$ in them. Further various other properties are discussed here.

Acknowledgements. Authors thank Tosoh F-Tech Co. for free samples.



Scheme 1

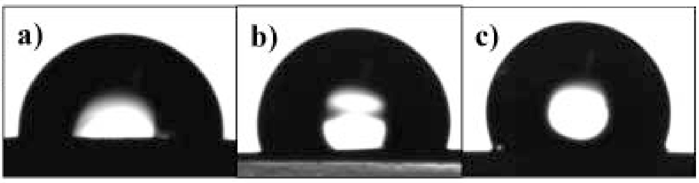


Figure 1

***Scheme 1.*** *The reaction pathway to make MAF-RF and its free radical copolymerization with VDF is shown. i. SOCl2, reflux, 22 h; 60% ii. Pyridine, CH2Cl2, -20 °C, 4 h; 85% iii. 2 wt% Conc. H2SO4, reflux, 20 h; 55%.*
***Figure 1****. Also water-contact angle measurement pictures shown for films made up of a) Pure PVDF, (108±3°) b) Poly(VDF-Co-MAF-RF) with 7 mol% MAF-RF (109±3°) and c) Poly(VDF-Co-MAF-RF) (118±3°) with 41 mol% MAF-RF.*

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## P1.74

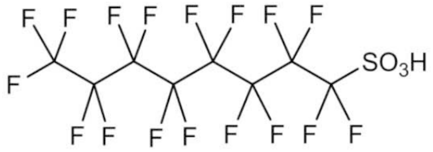
# Synthetic approach to new PFOS alternatives and their derivatives

**D.S. SHIN** [(a)]*, **B.V.D. VIJAYKUMAR** [(a)]

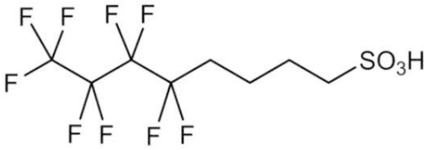
[(a)] CHANGWON NATIONAL UNIVERSITY, DEPARTMENT OF CHEMISTRY - CHANGWON (S. KOREA)

* dsshin@changwon.ac.kr

Perfluorooctanesulfonic acid (PFOS) 1 is well known surfactant having a $C_8$ -fluorocarbon chain attached to sulfonic acid group. All its derivatives are also showed surfactant activity and are the key ingredients in many stain repellents. PFOS related substances are proven to be hazardous and toxic to humans, animals and environment due to its non-biodegradability.[1,2] Global environmental pollution can be controlled by lessening the number of fluorine atoms in non-biodegradable fluorocarbon chain in those types of materials. Thus, we started working on $C_4$-perfluorocarbons to synthesize partially perfluosulfonic acid derivatives and compare their properties with PFOS analogs. Synthesis of a new surfactant 2 and their derivatives with less number of fluorine atoms to overcome some draw backs of PFOS, has been achieved by using a conjugate radical addition of partially perfluoroalkyl halides to phenylvinylsulfonate in ionic liquid and also in formamide.



Perfluorooctanesulfonic acid (**1**)



Nonafluorooctanesulfonic acid (**2**)

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## P1.75

# Controlled Radical Polymerization vs Conventional Radical Polymerization. Differences in Surface Properties of 4’-Nonafluorobutyl Styrene Polymers

**F. CERETTA** [(a)] , **A. ZAGGIA** [(a)*], **L. CONTE** [(a)], **B. AMEDURI** [(b)]

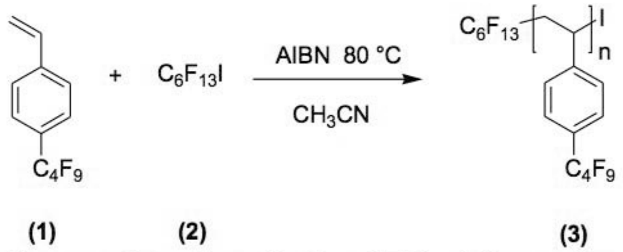
[(a)] Università degli Studi di Padova, LABORATORIO SULLA CHIMICA DEL FLUORO - PADOVA (ITALY)
[(b)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)

* alessandro.zaggia@unipd.it

4’-Nonafluorobutyl styrene was synthesized and polymerized by conventional and controlled radical polymerization (CRP) [1] based on iodine transfer polymerization (ITP) technique. Controlled free radical polymerization enabled to synthesize well-defined polymers with predictable molar masses and narrow poly-dispersity [2].

The fluorinated monomer was prepared from Ullmann coupling between 1-iodoperfluorobutane and 4’-nonafluorobutyl acetophenone followed by a reduction and a dehydration in overall 50% yield. The polymerization was initiated by AIBN and controlled by 1-iodoperfluorohexane in 84% monomer conversion and in 50% yield. The benefits of ITP of 4’-nonafluorobutylstyrene featured (i) a fast monomer conversion, (ii) the evolution of the $\ln([M]_0/[M])$ *versus* time that evidenced a linear behavior. The square of the propagation rate to the termination rate ($k_p^2/k_t$) of 4’-nonafluorobutyl styrene in ITP conditions was assessed ($3.66 \bullet 10^{-2}$ l • mol$^{-1}$ • sec$^{-1}$ at 80 °C) according to the Tobolsky’s kinetic law. The polydispersity index of fluoropolymer achieved by conventional polymerization was 1.30 while it was reduced to 1.15 for that synthesized by the controlled way. Contact angles and surface energies assessed on surface evidenced the influence of the PDI values with the surface properties of the synthesized polymers.

Surprisingly 4’-Nonafluorobutyl styrene polymers obtained by conventional radical polymerization (PDI = 1.30) showed better surface properties than those obtained by ITP (PDI = 1.15) in agreement with recent findings on the influence of molecular weight dispersity of poly[2-perfluorooctyl)ethyl acrylates][3].



**Scheme 1**. Iodine transfer polymerization (ITP) of 4’-nonafluorbutyl styrene (1) in presence of 1-iodoperfluorohexane (2) as the chain transfer agent.

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## P1.76

# The laboratory-scale preparation and suspension polymerization of TFE prepared by pyrolysis of PTFE waste and cryogenic distillation

**P. CROUSE [a]*, M. MABUDAFHASI [a]*, T. KILI [a], J. VAN DER WALT [b], C. THOMPSON [b]**

[a] UNIVERSITY OF PRETORIA - PRETORIA (SOUTH AFRICA)
[b] NECSA - PRETORIA (SOUTH AFRICA)

* philip.crouse@up.ac.za

Results are presented pertaining to the laboratory-scale synthesis of PTFE using scrap PTFE as the monomer source. The commercial production of TFE is usually effected by the well-known direct pyrolysis of R22 (CHClF2) [1]. For this work, the TFE was prepared by depolymerization of unfilled PTFE waste [2]. The reason for this was availbility locally of large qunatities of the material. The pyrolytic decomposition of PTFE yields a mixture which contains predominantly tetrafluoroethylene (TFE), hexafluoropropylene (HFP), octafluorocyclobutane (OFCB), perfluoroisobutylene (PFIB), and hexafluoroethane (HFE). The product distribution depends on the conditions under which the pyrolytic decomposition is performed. The pyrolysis gas-mixture was triple rectified in a Podbielniak-type cryogenic distillation column. It was found that better than 99.99% TFE purity is required for consistent yields. Polymerization results are reported for 11, 16, 21, and 27 bar runs using ammonium persulfate as initiator in a 300 mL laboratory reactor, at temperatures varying between 45 to 75 ºC. Molecular weight and degree of crystallinity were determined by standard calorimetric methods [3]. The DSC traces indicated bimodality of the heat of fusion, correlating with the crystallinity. This bimodality is more pronounced at higher pressures. The variation of polymer physical properties as function of geometric position inside reactor is shown. Safe handling of TFE was addressed via the SHEQ guidelines of the South African Nuclear Energy Corporation (Necsa).

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## P1.77

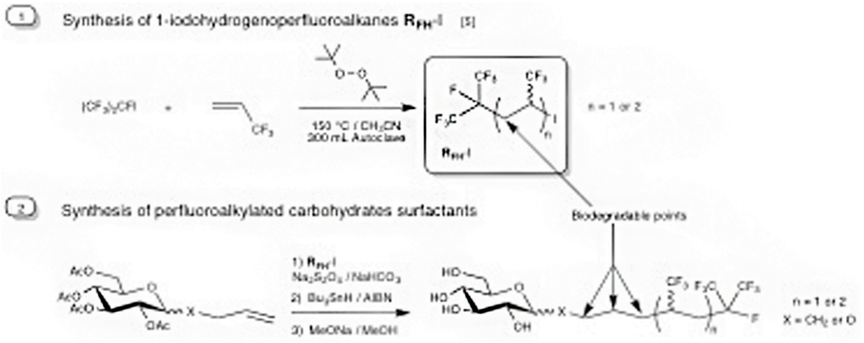
# Synthesis and Physicochemical Properties of Perfluoroalkylated Carbohydrates Surfactants Potentially Non-Bioaccumulable

**G. LOPEZ [a], M.N. WADEKAR [a], J. VELAY [a], B. AMEDURI [a]***

[a] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)

* Bruno.ameduri@enscm.fr

Fluorinated surfactants are surface-active agents comprised mainly of two structural components, an oleophobic perfluorinated carbon chain and a hydrophilic moiety. The latter part (anionic, cationic, amphoteric or non-ionic) is functionalized for selective applications. [1]. Due to the unique properties of the fluorine atom, fluorinated surfactants reduce surface-tension energy much more efficiently than their hydrocarbonated counterparts. Since the production of the first perfluoroalkyl carboxylates in 1947, fluorinated amphiphilic compounds have gained strategic importance in many applications of our everyday life [2]. However these compounds arouse concerns, since many of them exhibit the characteristics defined for persistent organic pollutants: they are toxic, persistent [3], and extremely resistant to degradation. This arises from the high stability of perfluorinated chains, which cannot undergo degradation, neither enzymatically, nor by metabolic pathways [4]. Moreover, fluorinated surfactants may accumulate in food chains and they may have long half-lives in human blood. This poster describes the synthesis of carbohydrate-based F-surfactants containing methylene units that interrupt the perfluoroalkyl chain, thus constituting some potential sites of degradability. The surface activities of these potentially non-bioaccumulable F-surfactants will also be discussed.



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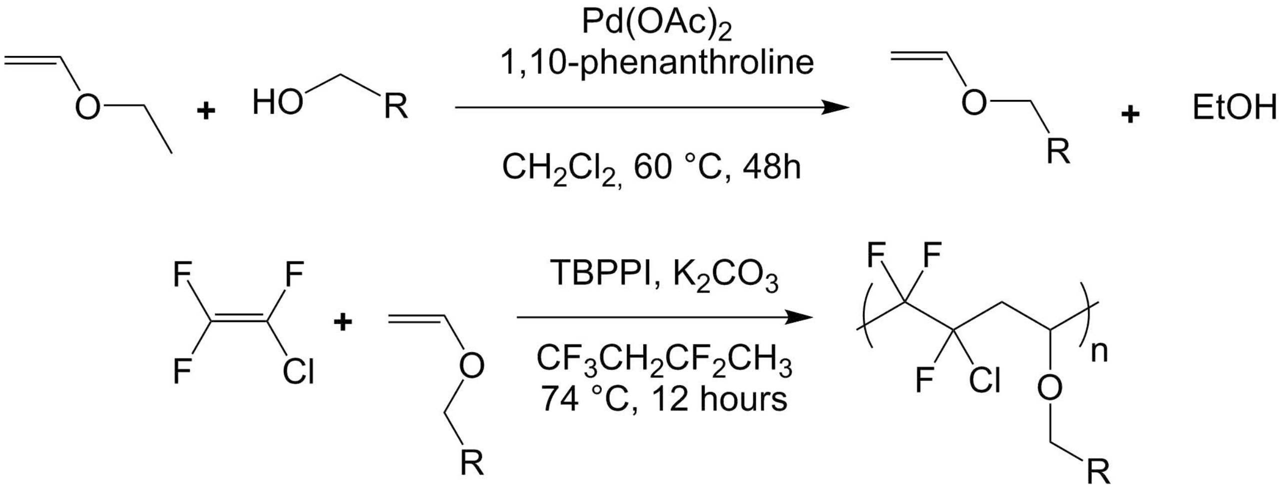
## P1.78

# Copolymerization, functionalization and characterization of poly(chlorotrifluoroethylene-*alt*-vinyl ether) copolymers

**G. COUTURE** [(a)]*, **A. ALAAEDDINE** [(a)], **S. ROUALDÈS** [(b)], **B. AMEDURI** [(a)]
[(a)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)
[(b)] Institut Europeen des Membranes - MONTPELLIER (FRANCE)
* guillaume.couture@enscm.fr

Among fluorinated polymers, poly(chlorotrifluoroethylene) (poly(CTFE)) exhibits remarkable gas barrier, inertness and film-forming properties [1]. However, because of the high cristallinity rate of PCTFE, CTFE has been copolymerized with various comonomers such as ethylene, styrene, vinyl acetate or methyl methacrylate [2]. Following the pioneer work of Tabata and DuPlessis [3], vinyl ethers (VEs) have been considered as interesting candidates as they form alternating copolymers with CTFE, giving rise to soluble, highly functionalizable materials. This presentation first presents the synthesis of original vinyl ethers via palladium-catalysed transetherification of ethyl vinyl ether [4]. The monomers were characterized by 1H and 13C NMR spectroscopy andwere then copolymerized with chlorotrifluoroethylene in 1,1,1,3,3-pentafluorobutane, initiated by tert-butylperoxypivalate at 74 °C. The structure of the obtained materials was determined via 1H and 19F NMR spectroscopy, and their properties were assessed by size exclusion chromatography, thermogravimetric analyses and differential scanning calorimetry.



*Synthesis of vinyl ethers via palladium-catalyzed transetherification and radical copolymerization of the obtained monomers with chlorotrifluoroethylene. R = -$(CH_2)_2$-Cl, -$CH_2$-$C(CH_3)_2$-$CH_2$-Cl, -$CH_2$-$C(CH_3)_2$-$CH_2$-$N(CH_3)_2$, -$CH_2$-$C(CH_3)_2$-$CH_2$ -N+$(CH_3)_3$.*

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## P1.79

# Precise Characterization of Molecular Aggregation State of Poly(perfluorooctylethyl acrylate) Immobilized on Nano-textured Film

**T. SHINOHARA** [(a)]*, **R. ISHIGE** [(b)], **Y. HIGAKI** [(b)], **Y. OKAMOTO** [(c)], **T. AOKI** [(c)], **A. TAKAHARA** [(b)]

[(a)] Graduate School of Engineering, WPI-I2CNER, Kyushu University, TAKAHARA LAB. - FUKUOKA (JAPAN)
[(b)] Institute for Materials Chemistry and Engineering, Kyushu University - FUKUOKA (JAPAN)
[(c)] DENSO Corporation - KARIYA, AICHI (JAPAN)

* shinohara@cstf.kyushu-u.ac.jp

Poly(perfluoroalkyl acrylate) (PFA-$C_8$) with long fluoroalkyl ($R_f$) side chains is a semi-crystalline polymer that has superior material characteristics *e.g.* water repellency, a low friction coefficient. Surface nano-structure enhances the water repellency caused by the Cassie-Baxter (CB) state. However, the molecular aggregation state of PFA-$C_8$ immobilized on nano-textured surface has not been evaluated. In this study, the PFA-$C_8$ brushes were fabricated on surface nano-textured polymer films, and the molecular aggregation state of $R_f$ group was evaluated by grazing incidence X-ray diffraction (GIXD).

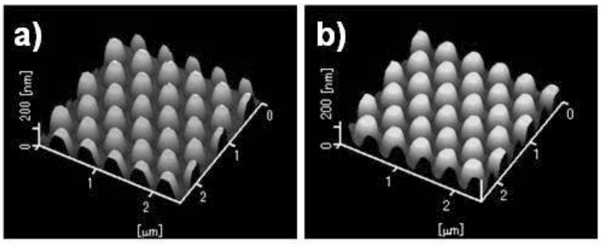

**Fig. 1** AFM images of a) NI_ P(MMA-*co*-BIEM) and b) NI_PFA.

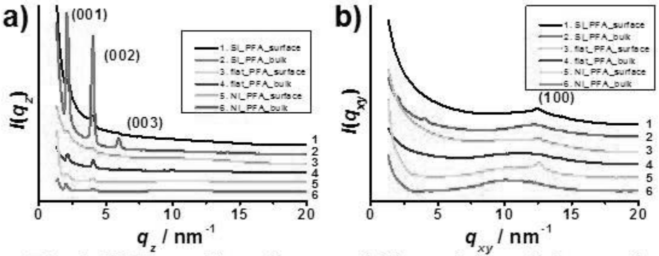

**Fig. 2** GIXD profiles of prepared films, a) out-of-plane and b) In-plane directions.

Poly[methyl methacrylate-*co*-{2-(2-bromoisobutyryloxy) ethyl methacrylate}] (P(MMA-*co*-BIEM)), which is a PMMA derivative with initiate group for surface initiated atom transfer radical polymerization (SI-ATRP), was spin casted on Si wafer (flat_P(MMA-*co*-BIEM)). A 230 nm pillar pattern was fabricated on the surface of flat_P(MMA-*co*-BIEM) by nano-imprint technique (NI_P(MMA-*co*-BIEM)). FA-$C_8$ was grafted from the flat_ and NI_P(MMA-*co*-BIEM) by SI-ATRP (flat_/NI_PFA). The surface properties and molecular aggregation state were evaluated by atomic force microscopy (AFM) observation, water contact angle measurement and GIXD.

The surface nano-texture was retained even after surface grafting of PFA-$C_8$ with *ca.* 60 nm brush thickness (Fig. 1). Water contact angle of NI_PFA was over 150°. This super-hydrophobicity was caused by the synergetic effect of hydrophobicity of $R_f$ group and the CB states. Fig. 2 shows the GIXD profiles of PFA-$C_8$ brush on P(MMA-*co*-BIEM) and Si wafer (Si_PFA). GIXD profiles were obtained from the surface and deeper regions at grazing angle 0.08° and 0.16°, respectively. Each samples had peaks around $q_z = 2$, 4, 6 $nm^{-1}$ in out-of-plane GIXD profiles (Fig. 2-a.). These peaks are assignable to a high-order diffraction pattern due to the lamellar structure of the $R_f$ groups oriented parallel to substrate [1]. For in-plane direction, peaks around the $q_{xy} = 12.6$ $nm^{-1}$ was observed only in the surface region (Fig. 2-b.). These peaks indicate that the rigid rod-like $R_f$ groups formed hexagonal packing in the surface regions of the films [1]. PFA-$C_8$ forms the same molecular aggregation states regardless of the surface nano-texture, indicating that the surface nano-texture makes no effect on the molecular aggregation state of PFA-$C_8$ brush in this system.

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[1] K. Honda, A. Takahara *et al.*, *Macromolecules*, **38** (2005) 5699-5705.

## P1.80

# Synthesis of trifluoroethylene (TrFE)

**M. GALIMBERTI [a]*, S. MILLEFANTI [a], C. MONZANI [a], V. TORTELLI [a], I. WLASSICS [a]**

[a] SOLVAY SPECIALTY POLYMERS - BOLLATE (MI) (ITALY)

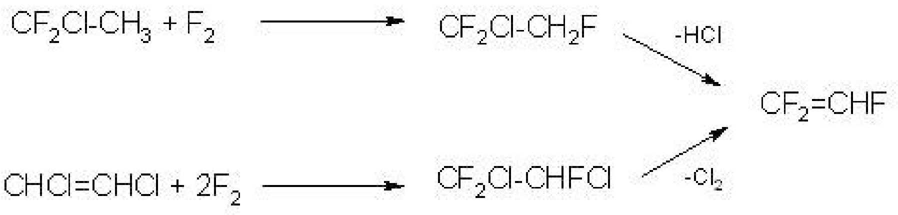
* marco.galimberti@solvay.com

Printed organic or hybrid organic/inorganic electronics has emerged as a promising technology for low-cost, large-area microelectronic applications where flexibility and lightweight are required. Solvay Specialty Polymers has developed in the last decade, a proprietary technology, allowing a polymerization process fully scalable at industrial level[1]. With this process, Solvay Specialty Polymers is in the right position to supply VDF/TrFE copolymers that are piezo, pyro and ferro electric polymers to the growing Printed Electronic industry.

At the same time we have been studying the TrFE comonomer synthesis, leveraging on our proprietary technology of fluorination, to find an internal solution and have an alternative to the availability of the monomer on the market.

Two synthetic routes will be described in this poster contribution, both based on a partial fluorination of selected HCFC with elemental fluorine[2]. The first one is based on the fluorination of CFC 142b to obtain CFC 133b, which is then dehydrochlorinated to TrFE; the second one starts from 1,2 dichloroethylene, fluorination to obtain CFC 123a, which after dechlorination gives TrFE. The two synthetic strategies are depicted in the figure.

The influence of the main operative parameters on conversion and selectivity of reactions will be presented and discussed.



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[1] US patent application 20110082271 (to Solvay Specialty Polymers) 2011

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## P1.81

# Decomposition of perfluorooctanoic acid photocatalyzed by titanium dioxide: chemical modification of the catalyst surface induced by fluoride ions

**F. PERSICO** [a]*, **M. SANSOTERA** [a], **W. NAVARRINI** [a], **C. BIANCHI** [b], **S. GATTO** [b], **C. PIROLA** [b]

[a] POLITECNICO DI MILANO, FLUORITECH - MILANO (ITALIA)
[b] UNIVERSITA DEGLI STUDI DI MILANO - MILANO (ITALIA)

* fpersico@chem.polimi.it

PFOA photomineralization by $TiO_2$ was tested in different conditions and monitored by Total Organic Carbon (TOC) and Ionic Cromatography (IC). TOC determined the trend of the carbon content in solution and IC measured the amount of fluoride ions generated during PFOA abatement [1]. The chemical composition of the photocatalyst was monitored by X-ray Photoelectron Spectroscopy (XPS) to evaluate variations occurred during the process. The experimental apparatus was a water-cooled glass stirred reactor equipped with a low-pressure UV lamp. A stock solution of PFOA (0.1 M) was prepared and diluted to chosen concentrations. The nanometric powder of $TiO_2$ was introduced in the reactor at the beginning of each test. The variation of [PFOA] in solution was monitored collecting samples at different reaction times [2]. For each sample, XPS survey and high resolution analyses in the typical zone of C-1s, Ti-2p, O-1s and F-1s were performed.

The PFOA photodegradation kinetics followed a pseudo-first order trend that enabled to compare the kinetic apparent constants ($K_{app}$). Three different values of the Kapp were observed changing the surfactant concentration; with [PFOA] higher than the CMC, the lowest mineralization rates were obtained (17% after 6h); at the CMC higher mineralization values were observed (24% after 6h), while with [PFOA] lower than the CMC a further increase in the mineralization rate was noticed (30% after 6h). XPS analyses of the catalyst samples showed no variation on $TiO_2$ surface in the first four hours of photoabatement, while considerable differences were noticed after nine hours. The presence of different titanium fluorides, together with pure titanium dioxide, was detected on the catalyst surface.

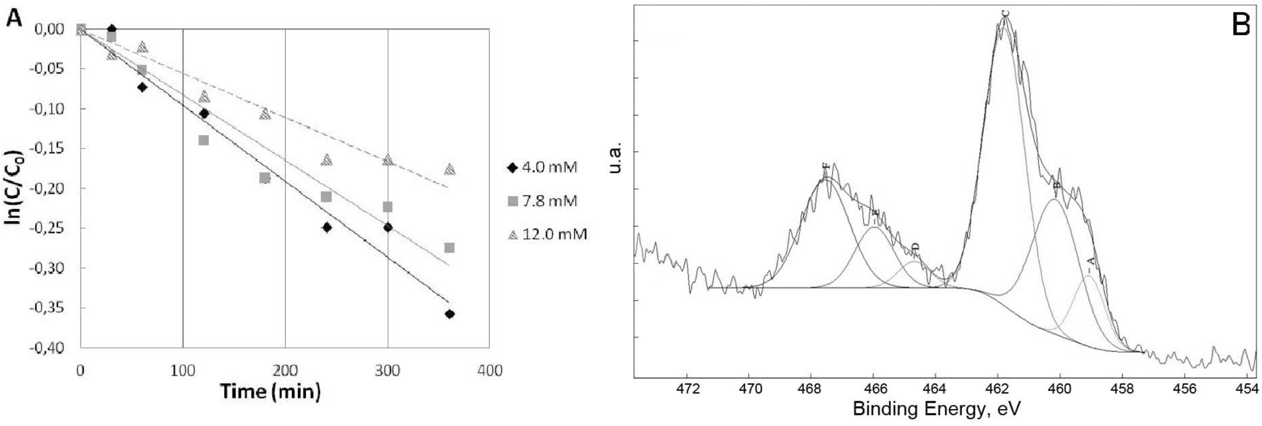

*Fig. 1. Linearized PFOA degradation curves (A); Ti 2p region XPS spectrum (B) of TiO2 after 9h photodegradation.*

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[1] S.C. Panchangam, A.Y.C. Lin, J.H. Tsai, C.F. Lin, *Chemosphere* **75** (2009) 654-660.

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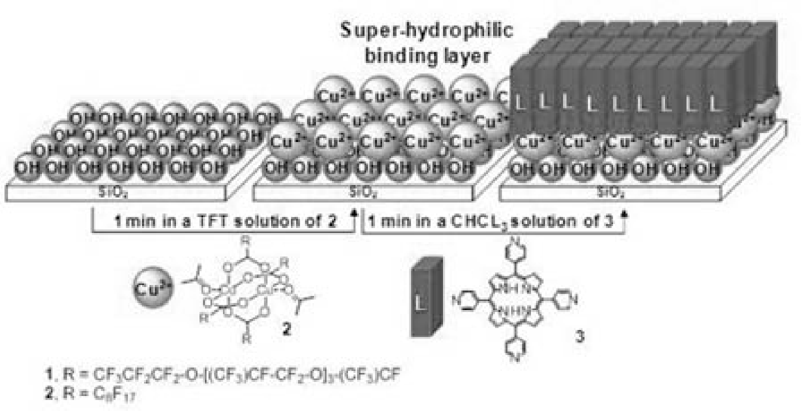
## P1.82

# Adsorption of fluorous copper(II)-carboxylate complexes onto Teflon or glass: straightforward preparation of super-hydrophilic and coordinating surfaces

**J.M. VINCENT** [a]*, **G. RAFFY** [a], **A. DEL GUERZO** [a], **A. MOTREFF** [b], **C. BELIN** [a]

[a] CNRS - UNIVERSITÉ DE BORDEAUX, INSTITUT DES SCIENCES MOLÉCULAIRES - TALENCE (FRANCE)
[b] School of chemistry - ST ANDREWS (UNITED KINGDOM)

* jm.vincent@ism.u-bordeaux1.fr



Methodology based on coordination chemistry are emerging as powerful tools for the preparation of mono- and multilayers assemblies providing in some cases, a high control of molecular ordering in the resulting films.[1]

We discovered recently that the dicopper(II) complex 2, in which the perfluorinated chain is directly appended to the carboxylate group, exhibit an extremely high affinity for water in the solid state.[2] Adsorption of 1 or 2 onto materials such as Teflon [3] or glass [4] strongly affect their surface properties as it leads to surfaces exhibiting both super-hydrophilic and coordinating properties. For instance, complexes 1 or 2 are readily chemisorbed on $SiO_2$ surfaces providing binding copper(II) monolayers which could be further functionalized by non-fluorophilic pyridyl-tagged compounds like the *meso*-tetra(4-pyridyl)porphyrin 3 (scheme below).

In the poster, the preparation of the modified surfaces, their characterization (AFM, SEM, fluorescence microscopy, contact angles...), wettability and binding properties will be described.

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[3] Motreff, A.; Belin, C.; Correa da Costa, El Bakkari, M.; Vincent, J.-M. *Chem. Commun.* **2010**, *46*, 6261-6263.
[4] Motreff, A.; Raffy, G.; Del Guerzo, A.; Belin, C.; Dussauze, M.; Rodriguez, V.; Vincent, J.-M. *Chem. Commun.* **2010**, *46*, 2617-2619.

## P1.83

# Surfactants with low Fluorine Content

**J. EL MAISS [(a)], M. WOLFS [(b)]*, E. TAFFIN DE GIVENCHY [(a)], F. GUITTARD [(a)]**

[(a)] University of Nice Sophia Antipolis - NICE (FRANCE)
[(b)] University of Nice Sophia Antipolis, SURFACES AND INTERFACES RESEARCH GROUP - LPMC - NICE (FRANCE)

* Melanie.WOLFS@unice.fr

Fluorinated surfactants are truly the "Super Surfactants". Due to the unique properties of the fluorine atom, these fluorinated surfactants can reduce the surface tension energy much more than that achievable by hydrocarbon-type surfactants. They can distinguish themselves by their exceptional chemical stability in corrosive media and they can be used in media where conventional surfactants do not survive.

Because of their capacity to low surface tension, "Low Surface Energy Materials" made by fluorinated surfactants are innovative being both hydrophobic and oleophobic, also indispensable in certain practical applications such as printing, painting, adhesion, emulsification…The wide utilization due to the ability to control surface properties have several disadvantages specially bio-persistence, bio-accumulation[1] and high cost. This will allow development of a new generation of environmentally responsible and cost efficient materials.

This project is centred on intelligent programmed molecular design of surfactants with low fluorine contents neither non fluorinated ones, or at last, will generate similar surface properties to the undesirable Fluorocarbons. Recent results [2], [3] have demonstrated that structural modification of hydrocarbon chains gives rise to dramatic reductions surface energy, notably even in the absence of Fluorine.

Our project involves the design and synthesis of hydrocarbons surfactants replacing hazardous FC-surfactants having comparable surface tension energy with fluorinated homologues in the aim of limiting several impacts on environment. We will present their synthesis and their physico-chemical properties

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## P1.84

# Wetting Properties Designed With Long Or Two Short Fluoroalkyl Chains

**A. DRAME [a], M. WOLFS [b]*, E. TAFFIN DE GIVENCHY [a], S. AMIGONI [a], T. DARMANIN [a], F. GUITTARD [a], S. DIENG [c], M. OUMAR [c], A. DIOUF [c], D. FAYE [c], D. DIOUF [c]**

[a] University of Nice Sophia Antipolis - NICE (FRANCE)
[b] University of Nice Sophia Antipolis, SURFACES AND INTERFACES RESEARCH GROUP - LPMC - NICE (FRANCE)
[c] Université Cheikh Anta DIOP - DAKAR (SÉNÉGAL)

* Melanie.WOLFS@unice.fr

Fluorinated surfactant, are of growing interest, as they are known to combine particular surface properties generally induced both by the fluorinated tail and the gemini structure (two tailed surfactants) without facing the low water solubility often encountered for highly fluorinated compounds [1,2]. Since the bioaccumulation of perfluorinated acid with long fluoroalkyl chain ($C_x \geq 8$, where x is the number of fluorinated carbons) is becoming a serious concern, it is necessary to design fluoropolymer and fluorosurfactant coating with short fluoroalkyl chain [3].

The interest of this work is to observe aggregation structure in aqueous solution of new anionic original compounds with one long, or two short fluorinated tails. These surfactants were synthesized and characterized, using the measurement of critical micellar concentration (CMC) and surface tension by the mean of the Kruss K100 tensiometer. The tuning of the length of the one or two fluorinated chains was used to optimize the aggregation properties that are highlighted by TEM studies.

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[2] S.Y. Dieng, S. Szonyi, M. Jouani, H.J. Watzke, A. Cambon, *Colloids Surf.*, **98** (1995) 43.
[3] F. Suja, B.K. Pramanik, S.M. Zain, *Water Sci. Technol.*, **60** (2009) 1533.

P1.85

# Superhydrophobic Coatings Using Perfluoronated Halloysite Nanotubes

**W. MA** [(a)]*, **Y. HIGAKI** [(b)], **A. TAKAHARA** [(b)]

[(a)] International Institute for Carbon-Neutral Energy Research (WPI-I2CNER),KYUSHU UNIVERSITY - FUKUOKA (JAPAN)
[(b)] Institute for Materials Chemistry and Engineering, Kyushu University - FUKUOKA (JAPAN)

* m-wei@cstf.kyushu-u.ac.jp

Nanotubular materials are important building blocks for future nanotechnology and have attracted research interests over the past two decades. Among various nanotubes, an increasing attention has been being paid to the clay based ones, due to many of their great advantages, such as abundant availability, environmental friendliness, and biocompatibility. One of the most well-known clay nanotubes is halloysite, a hydrated polymorph of kaolinite consisting of silica on the outer surface and alumina in the innermost surface [1]. Halloysite has been widely used as nanocontainers for controlled release of various active agents and nanofillers for organic/inorganic hybrid materials. Other usages of halloysite include pollutant removing, catalyst supporter, and drug delivery.

Superhydrophobic surfaces with water contact angle larger than 150° have shown great significance in both scientific and industrial areas, due to their potential applications in many important areas, including self-cleaning materials, corrosion resistance, and low dragging coatings [2]. By mimicking lotus structure, a considerable amount of artificial superhydrophobic surfaces have been developed. However, most of the reported methods require special equipment, complicated process control or expensive materials. Superhydrophobic surfaces using clay nanotubes as the building blocks have not been reported.

In this work, we demonstrated the fabrication of a superhydrophobic coating using 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (FOTMS) modified Halloysite nanotubes (F-HNT). A sol-gel process using tetraethoxysilane (TEOS) and F-HNT was applied for the coating preparation. Fourier transform infrared (FTIR) analysis indicated that halloysite nanotubes were successfully modified with FOTMS. SEM measurements show that the F-HNT/silica coating exhibited a micro/nano hierarchical structure (Fig. 1a). The obtained coating gives water contact angles above 150° (Fig. 1b). Moreover, the hydrophobicity of the film can be tuned by the content of F-HNT; stick and non-sticky superhydrophobic films can also be achieved at certain F-HNT contents.

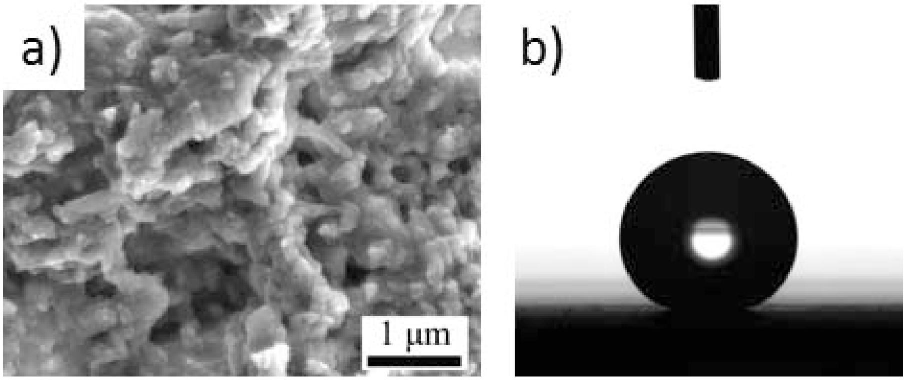

*Fig. 1. (a) SEM image of F-HNT/silica film containing 60 wt% F-HNT. (b) Micrograph of a water droplet on this film.*

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## P1.86

# Development of a multi-purpose laboratory-scale fluoropolymer facility

**P. CROUSE [(a)]*, P. SONNENDECKER [(a)]***

[(a)] UNIVERSITY OF PRETORIA - PRETORIA (SOUTH AFRICA)

* philip.crouse@up.ac.za

The Fluoro-Materials Group, within the Department of Chemical Engineering at the University of Pretoria recently initiated a number of fluoropolymer-based research activities, with the financial support of the South African Department of Science and Technology. Work commenced at the South African Nuclear Energy Corporation, and was performed under their existing SHEQ system. The activity moved to the university campus in 2012 when the Group obtained space for a new laboratory where all the various pieces of equipment (PTFE pyrolysis, rectification, polymerization) are being be integrated into one safe, automated, computer-controlled system.

The depolymerisation system is operated at the conditions proposed by Lewis and Naylor [1] and is capable of producing high purity TFE suitable for re-polymerisation, without the need for separation by batch distillation. The system consists of a high-temperature reactor (controlled at ~650 °C and below 500 Pa abs.) and a condenser to maintain the vacuum in the system. The reactor is also designed to accommodate the thermal decomposition of $CF_3CF_2CO_2M$ to produce TFE and $CO_2$ [2], to be used in the production of PTFE via the super-critical $CO_2$ method [3], and as safer source of TFE.

The remainder of the apparatus consists of a batch cryogenic distillation column designed for the separation of hexafluoropropylene, octafluorocyclobutane and TFE (should the need arise), and two stirred batch reactors, purchased from Parr Instrument Co. The reactor system is designed to be as versatile as possible, and to accommodate the production of PVDF, FEP, and other co-polymers with TFE.

The current status of the project is reported here.

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## P1.87

# Self-healing PFPE-based Materials

**G. MARCHIONNI [a]*, S. PETRICCI [a], S. BARBIERI [a], C. TONELLI [a]**

[a] SOLVAY SPECIALTY POLYMERS, R&T CAMPUS - BOLLATE (ITALY)

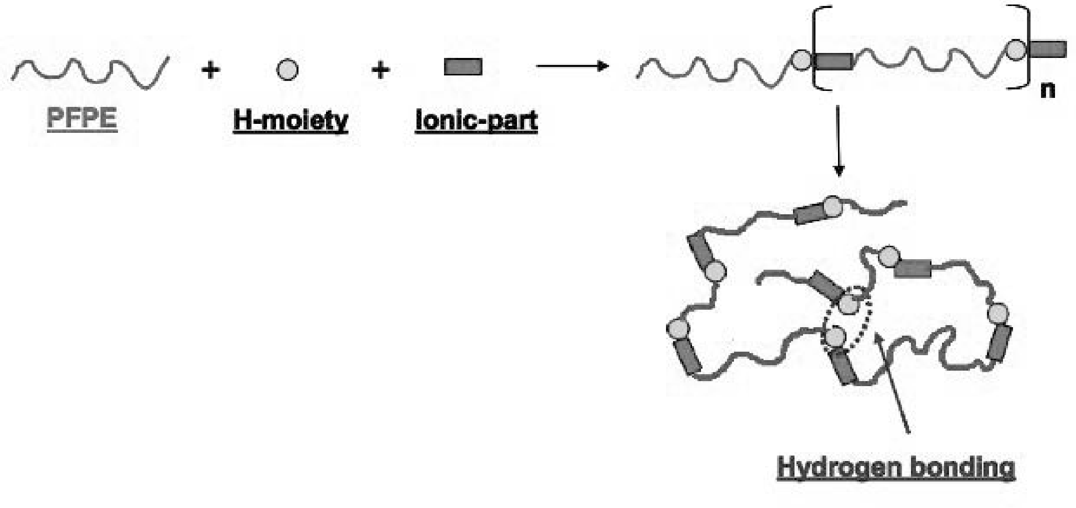
* Giuseppe.marchionni@solvay.com

In the broadest meaning, sustainability is the capacity to endure. Nature offers many examples of sustainable biological systems: for example the human body's ability to heal wounds by sending blood platelets to the affected area already represents a good template to develop innovative materials able to close cracks in their structures without external help.

Solvay Specialty Polymers has been developing a new family of Fluorinated polymers having hydrogen bonded and ionic bonded chains and characterized by a paramount self-healing (SH) ability. The original synthetic approach [1, 2] arises from the proprietary Perfluoropolyethers (PFPEs) technological platform and combines in a tridimensional physically interconnected network the unique properties of the fluorinated materials with automic self-healing ability.

Unlike other H-bonded SE polymers, these materials do not require any kind of plasticizer, or thermal treatment, because they have a very low Tg, that brings high chain mobility at room temperature. Moreover, it should be expected that they will offer other extra advantages due to their highly fluorinated structure: chemical resistance, and unique surface properties among others.

This strategic approach and some base property-structure relationships have been defined and validated to support the development of tailored materials for high demanding market sectors.



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[1] Solvay Specialty Polymers International application WO 2013/017401

[2] Solvay Specialty Polymers International application WO 2013/017470

## P1.88

# Fluorination of surface of chemically modified silicas

**I. BOLBUKH** [(a)*], **P. KUZEMA** [(a)], **B. MISCHANCHUK** [(a)], **V. TERTYKH** [(a)], **E. DURAND** [(b)], **A. TRESSAUD** [(b)]

(a) INSTITUTE OF SURFACE CHEMISTRY OF NAS OF UKRAINE, CHEMISORPTION - KYIV (UKRAINE)
(b) ICMCB-CNRS - PESSAC (FRANCE)

* yu_bolbukh@yahoo.com

As known, fluorination of silica surface with HF, $NH_4F$, $F_2$, $BF_3$ results in formation of hydrolytically labile silicon-fluorine bonds. There is a great interest to graft on the silica surface fluorocarbons with stable C-F bonds in order to prepare appropriate fillers for fluorine-containing polymers and materials with increased hydrophobic properties. We apply for this purpose the radiofrequency plasma-enhanced fluorination of silicas with chemically modified surface.

Fluorination of fumed silica with various grafted functional groups was performed by c-$C_4F_8$ RF plasma at 25°C and 100 mTorr. The silicas subjected to fluorination were: pristine $SiO_2$ and fumed silicas modified with triethoxysilane ($C_{Si\text{-}H}$ = 0.49 mmol/g), vinyltriethoxysilane ($C_{c=c}$ = 0.22 mmol/g) or vinyltrichlorosilane ($C_{c=c}$ = 0.47 mmol/g). Surface chemistry of the fluorinated silica samples was characterised by FT-IR spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption mass spectrometry.

The surface layer structure of the silylated silicas after plasma fluorination is defined by the reactivity of the pre-grafted groups. Itwasfound that for hydride- and vinyl-silylated silicas a long term (about 60 min) plasma treatment leads to formation of polymeric film at the surface, whereas at facile (about 15 min) treatment the single fragments with C:F ratio close to 1:1 are attached to surface as in the case of pristine silica fluorination. It should be noted that both the nature of pre-grafted groups capable to be involved in polymerization reaction and their concentration affect the polymeric film structure. Thus, at surface groups concentration of about 0.5 mmol/g fluorine-enriched polymeric chains are formed, while at twice as little concentration the chain with unsaturated bonds are generated.

Usually fluorination of silica surface in solutions containing fluoride ions is occurring *via* two stages: a nucleophilic substitution of OH groups by F atoms at low fluoride concentrations, and the opening of siloxane bonds at higher fluoride concentrations. In the case of plasma-enhanced fluorination with octafluorocyclobutane, the surface layer structure is determined by the destruction mechanism of fluorinating agent. Our experimental results show that after short-term (about 15 min) fluorination of pristine silica the surface mainly contains groups with two carbon atoms which testify the symmetrical decomposition of the fluorinating agent.

Dr. Christine Labrugère (CECAMA, ICMCB-CNRS) is acknowledged for XPS investigations and spectra fitting.

# POSTER SESSION 2

## WEDNESDAY, JULY 24

# Wednesday, July 24

# POSTER SESSION 2

**P2.1** COMBINATION OF RUTHENIUM COMPLEX, AMINO ALCOHOL AND i-PROH IN THE ENANTIOSELECTIVE TRANSFER HYDROGENATION OF $CF_3$-KETIMINES. SYNTHESIS OF ENANTIOENRICHED $CF_3$-AMINES x

X. Dai, **D. Cahard***

**Université de Rouen - CNRS, UMR 6014 COBRA, Mont-Saint-Aignan (France)*

**P2.2** CHIRAL BRØNSTED ACID-CATALYZED DIASTEREO- AND ENANTIOSELECTIVE SYNTHESIS OF $CF_3$-SUBSTITUTED AZIRIDINES x

Z. Chai, J.-P.-Bouillon, **D. Cahard***

**Université de Rouen - CNRS, UMR 6014 COBRA, Mont-Saint-Aignan (France)*

**P2.3** PREPARATION OF GEM-DIFLUOROMETHYLENE BUILDING BLOCKS THROUGH REGIOSELECTIVE ALLYLATION OF GEM-DIFLUOROCYCLOPROPANES

D. Munemori, T. Kawamura, S. Hayase, T. Nokami, **T. Itoh***

**Tottori University, Dept Chemistry & Biotechnologies, Tottori (Japan)*

**P2.4** PHOTOCHEMICAL PROPERTIES OF THE FLUORINE SUBSTITUTED PHOSPHAALKENES: QUANTUM CHEMICAL SIMULATIONS x

**V.I. Kharchenko***, L.N. Alexeiko

**Institute of Chemistry, Feb RAS, Laboratory of ESQCS, Vladivostok (Russia)*

**P2.5** NEW EXAMPLES OF RADICAL ADDITION OF BROMODIFLUOROMETHYL CONTAINING REAGENTS TO VINYL ETHERS

**I. Kondratov***, G. Posternak, N. Tolmacheva, I. Gerus, G. Haufe

**Institute of Bioorganic Chemistry and Petrochemistry, NUAS, Kiyv (Ukraine)*

**P2.6** SYNTHESIS OF NEW TRIFLUOROMETHYL CONTAINING PYRROLIDINES

**V. Dolovanyuk**, I. Kondratov*, N. Tolmacheva, I.I. Gerus, G. Haufe

**Institute of Bioorganic Chemistry and Petrochemistry, NUAS, Kiyv (Ukraine)*

**P2.7** NEW FLUOROALKYLATION REACTIONS INVOLVING FIRST ROW METALS

**D. Vicic***, Y. Budnikova, A. Klein

**Lehigh University, Dept of Chemistry, Bethlehem, Pa (USA)*

**P2.8** STEREO- AND REGIOSELECTIVE SYNTHESIS OF $\alpha$-FLUOROENAMIDES

**B. Metayer***, G. Compain, G. Evano, A. Martin-Mingot, S. Thibaudeau

**Université de Poitiers – CNRS, IC2MP - Groupe Superacide, Poitiers (France)*

**P2.9** FLUORINATED PHOSPHONATES, USEFUL SYNTHETIC BUILDING BLOCKS

**S. Opekar***, P. Beier

**IOCB, ASCR, Organic Synthesis, Prague (Czech Republic)*

**P2.10** FLUORINATED METAL ORGANIC FRAMEWORKS: SYNTHESIS AND PROPERTIES

**E. Magnier***, C. Yu, H. Ren, T. Devic, P. Horcajada, C. Serre, S Bourrelly, P. Llewellyn

**Université de Versailles-Saint Quentin-CNRS, ILV UMR 8180, Versailles (France)*

**P2.11** DEVELOPMENT OF NEW REAGENTS FOR TETRAFLUOROETHYL AND TETRAFLUOROETHYLENE GROUP TRANSFER

**Y. Chernykh***, P. Beier

**IOCB, ASCR, Praha (Czech Republic)*

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**D. Gladow***, H. Reissig

**FU Berlin, Institut für Chemie und Biochemie, Berlin (Germany)*

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**Sarl @rtMolecule, Organic Synthesis Team, Poitiers (France)*

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**Jacobs University Bremen, Scholl of Engineering & Science, Bremen (Germany)*

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**M.V. Ponomarenko***, Y.A. Serguchev, M.E. Hirschberg, G.V. Roeschenthaler, A.A. Fokin

**Jacobs University Bremen, Scholl of Engineering & Science, Bremen (Germany)*

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**P. Fedorov***, E. Chernova

**A.M. Prokhorov General Physics Institute, RAS, Laser Materials & Technology Research Center, Moscow (Russia)*

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**A. Prunier***, E. Pfund, J. Legros, J. Maddaluno, T. Lequeux

**Ecole Nationale Supérieure d'Ingénieurs-Caen, Laboratoire de Chimie Moléculaire et Thio-Organique, Caen (France)*

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**Institute of Organic Chemistry, NAS of Ukraine, Kyiv (Ukraine)*

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**Université de Rouen, UMR CNRS 6014 COBRA, Mont-Saint-Aignan (France)*

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**Université de Savoie, LEPMI - UMR5279, Le Bourget-du-Lac (France)*

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**Tokyo University of Pharmacy & Life Sciences, School of Pharmacy, Tokyo (Japan)*

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*Department of Chemistry, Durham University - Durham (UK)

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**P. Holze***, C. Limberg
*Humboldt Universität zu Berlin, Berlin (Germany)*

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*Institute of Chemistry, Feb RAS, Fluoride Materials, Vladivostok, (Russia)*

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**N.I. Lobachevsky Nizhniy Novgorod State University, Dept of Macromolecular Chemistry & Colloid, Nizhniy Novgorod (Russia)*

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**Setsunan University, Lab of Pharmaceutical Chemistry, Hirakata (Japan)*

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**Chinese Academy of Sciences, Key Laboratory of Organofluorine Chemistry, Shanghai (China)*

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**T. Yajima***, M. Shinmen

**Ochanomizu University, Chemistry, Tokyo (Japan)*

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**G. Compain***, B. Linclau

**University of Southampton, Molecular Diagnostics & Therapeutics Section, Southampton (UK)*

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**CNRS, Lab. Chimie de Coordination, Toulouse (France)*

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**Faculté de Pharmacie Université Paris-Sud, BIOCIS, Châtenay Malabry (France)*

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**L. Lu**

*Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, CAS, Shanghai (China)*

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**N. Santschi***, A. Togni

**ETH Zürich, Institute of Inorganic Chemistry, Zürich (Switzerland)*

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**J. Goettel***, N. Kostiuk, M. Gerken

**University of Lethbridge, Chemistry & Biochemistry, Lethbridge (Canada)*

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**Institute of Chemistry, FEB RAS, Chemistry Lab; Rare Metals, Vladivostok (Russia)*

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**JSC «Leading Scientific Research Institute of Chemical Technology», Moscow (Russia)*

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**N. Laptash***, A. Udovenko

**Institute of Chemistry, Feb RAS, Vladivostok (Russia)*

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**M. R. Lichtenthaler***, I. Krossing

**University of Freiburg, Institute for Inorganic & Analytical Chemistry, Freiburg Im Breisgau (Germany)*

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**Jožef Stefan Institute, Dept Inorganic Chemistry & Technology, Ljubljana (Slovenia)*

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**Nikolaev Institute of Inorganic Chemistry, SB RAS, Lab. of Carbon Materials Chemistry, Novosibirsk (Russia)*

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**Bielefeld University, Anorganic Chemistry II, Bielefeld (Germany)*

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**FU Berlin, Anorganische Chemie, Berlin (Germany)*

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**NFMLAB-DCMIC "Giulio Natta", Politecnico di Milano, (Italy)*

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** NFMLAB-DCMIC "Giulio Natta", Politecnico di Milano (Italy)*

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**Lomonosov Moscow State University, Chemistry Dept, Moscow (Russia)*

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**Nagoya Institute of Technology, Dept of Frontier Materials, Nagoya (Japan)*

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**McMaster University, Dept of Chemistry, Hamilton, ON (Canada)*

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**Université de Poitiers – CNRS, IC2MP, Poitiers (France)*

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**Kanagawa University, Faculty of Science, Hiratsuka (Japan)*

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**FU Berlin, Organic Chemistry, Berlin (Germany)*

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**CNRS, CEA, Unicaen, UMR 6301 ISTCT - LDM-TEP, Caen (France)*

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**Institute of Chemistry, FEB RAS, Lab. of Protecting Coatings & Marine Corrosion, Vladivostok (Russia)*

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**Université de Strasbourg, Institut Charles Sadron – CNRS, Strasbourg (France)*

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**Department of Organic Chemistry, Prague (Czech Republic)*

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**Institute of Chemical Technology, Dept of Organic Chemistry, Prague (Czech Republic)*

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**Kitasato University, Dept. of Chemistry, Sagamihara (Japan)*

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**Tomsk Polytechnic University, Fluorine Chemistry & Engineering, Tomsk (Russia)*

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*DuPont de Nemours International, Chemicals & Fluoroproducts, Geneva (Switzerland)*

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**Universite Blaise Pascal, ICCF, Aubière (France)*

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**Université Blaise Pascal, ICCF, Aubière (France)*

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**Université Pierre et Marie Curie-CNRS, PECSA, Paris (France)*

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**Scientific Research Insitute of Chemical Technology, Moscow (Russia)*

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**Politecnico di Milano, Fluoritech, Milano (Italy)*

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**Université Pierre et Marie Curie-CNRS, PECSA, CNRS UMR 7195, Paris (France)*

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**Université Pierre et Marie Curie, PECSA, CNRS UMR 7195, Paris (France)*

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** Université Pierre et Marie Curie, CNRS UMR 7195, Paris (France)*

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**V. Tomina***, I. Melnyk, Y. Zub
*Chuiko Institute of Surface Chemistry, NAS of Ukraine, Surface Chemistry of Hybrid Materials, Kyiv (Ukraine)*

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*Institute of Bioorganic Chemistry & Petrochemistry, NAS, Kyiv (Ukraine)*

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**R. Senn***, A. Togni
**ETH Zürich, Laboratory of Inorganic Chemistry, Zürich (Switzerland)*

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**University of Fukui, Materials Science & Engineering, Fukui (Japan)*

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**University of Fukui, Materials Science & Engineering, Fukui (Japan)*

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**Institute of Chemistry, Feb RAS, Vladivostok, (Russia)*

**P2.82** **MINI REACTOR FOR THE DIRECT FLUORINATION OF ETHYLENCARBONATE**

**P. Zhang***, M. Hill , S. Goll , P. Lang, P. Woias, I. Krossing

**Institute for Inorganic and Analytical Chemistry, University of Freiburg, Freiburg (Germany)*

**P2.83** **[$^{18}$F]-FLUORINATION OF 4-[(HALOGENO OR SULFONYLOXY) METHYL] PIPERIDINES: A COMPARATIVE EXPERIMENTAL AND MECHANISTIC STUDY**

M. Keita, S. Schmitt, G. Dupas, R. Brown, **C. Perrio***

**CNRS-CEA-UCBN, LDM-TEP, UMR6301 ISTCT, CYCERON, Caen (France)*

**P2.84** **PHOTOINDUCED PERFLUOROALKYLATION OF 9-METHYL-ANTHRACENE**

**E. Nogami**, T. Yajima

**Ochanomizu University, Yajima Lab., Tokyo (Japan)*

**P2.85** **3D OPAL NANOSPONGE AND CARBONE-FLUORINE SPECTROSCOPY™: THE EMERGENCE OF NANOTRONICS™ AS POSSIBLE NANO-FLUORO-THERANOSTIC TOOL**

**F. Menaa***, B. Menaa, L. Avakyantz, O. Sharts

**Fluorotronics, Inc., Dept of Chemical Sciences, Nanomaterials & Nanobiotechnology, Carlsbad, CA (USA)*

## P2.1

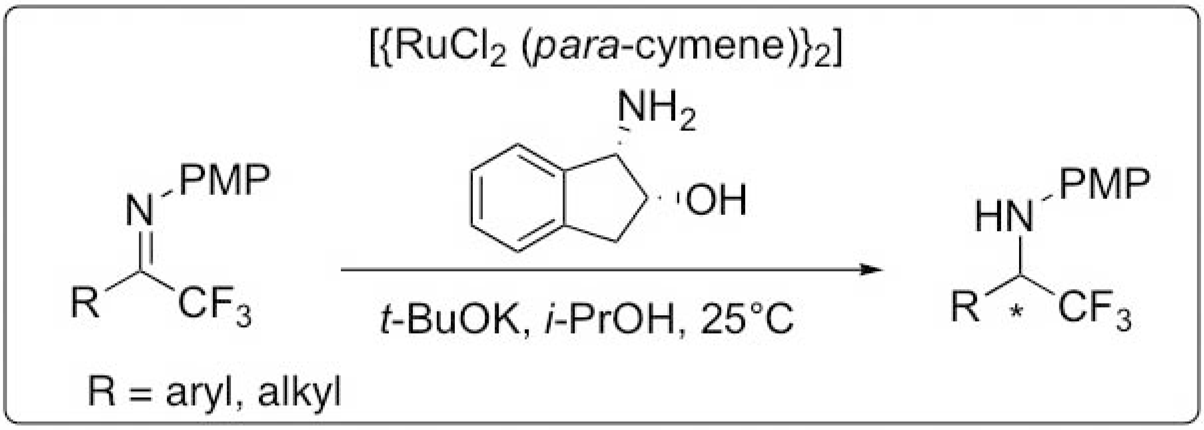
# Combination of ruthenium complex, amino alcohol and i-PrOH in the enantioselective transfer hydrogenation of $CF_3$-ketimines. Synthesis of enantioenriched $CF_3$-amines.

**X. DAI** [(a)], **D. CAHARD** [(b)]*

[(a)] INSA-ROUEN, IRCOF-FLUORINE CHEMISTRY - ROUEN (FRANCE)
[(b)] UNIVERSITÉ DE ROUEN, UMR CNRS 6014 COBRA - MONT SAINT AIGNAN (FRANCE)

* dominique.cahard@univ-rouen.fr

Chiral amines as structural features are widely present in natural products and synthetic biologically active compounds. Of particular importance is the sterecontrol of the asymmetric carbon centre bearing the $CF_3$ group and the amino function because biological activity and stereochemistry are closely related. Although many research groups have reported the asymmetric reduction of ketimines to obtain the corresponding chiral amines by transition-metal and organocatalysis, these methodologies applied to fluorinated ketimines have been much less investigated. In 2010, Zhou’s group reported a palladium-catalyzed hydrogenation of fluorinated imines under high pressure of hydrogen.[1] In the last decade, asymmetric transfer hydrogenation has attracted considerable attention because it is operationally simple. In 2011, Akiyama’s group introduced chiral phosphoric acid organocatalysts in the transfer hydrogenation of aromatic and heteroaromatic trifluoromethylated imines with excellent results.[2] However, to the best of our knowledge, the asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes has never been applied to the reduction of trifluoromethylated imines. Herein, we present the ruthenium-catalyzed enantioselective transfer hydrogenation of trifluoromethylated imines by using isopropanol as hydride source.



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P2.2

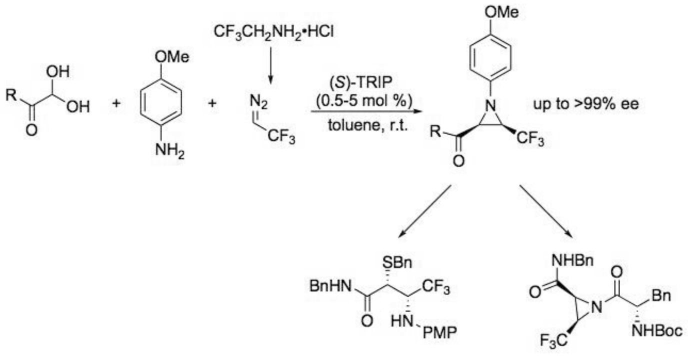
# Chiral Brønsted Acid-Catalyzed Diastereo- and Enantioselective Synthesis of $CF_3$-Substituted Aziridines

**Z. CHAI [(a)], J. BOUILLON [(a)], D. CAHARD [(a)]***

[(a)] UNIVERSITÉ DE ROUEN, UMR CNRS 6014 COBRA - MONT SAINT AIGNAN (FRANCE)

* dominique.cahard@univ-rouen.fr

A multicomponent organocatalyzed highly diastereo- and enantioselective synthesis of $CF_3$-substituted aziridines is described. This reaction of in situ generated $CF_3CHN_2$ and aldimines was realized by chiral Brønsted acid catalysis. The utility of the products is illustrated in easy access to *b*-$CF_3$ isocysteine and aziridine-containing dipeptides.[1]



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## P2.3

# Preparation of gem-Difluoromethylene Building Blocks through Regioselective Allylation of gem-Difluorocyclopropanes

**D. MUNEMORI [(a)], T. KAWAMURA [(a)], S. HAYASE [(a)], T. NOKAMI [(a)], T. ITOH [(a)]***

[(a)] Itoh Labo, Department of Chemistry and Biotechnology, Tottori University - TOTTORI CITY (JAPAN)

* titoh@chem.tottori-u.ac.jp

Much attention has thus been given to the preparation of gem-difluoromethylene derivatives as a source for novel functional materials. Syntheses of gem-difluoromethylene compounds were generally achieved by the difluorination of carbonyl or thiocarbonyl functional group. However, since fluorination reagents are limited and expensive, a synthetic strategy using a building block which has a gem-difluoromethylene moiety has also been recognized as a very attractive route to accessing gem-difluoromethylene compounds

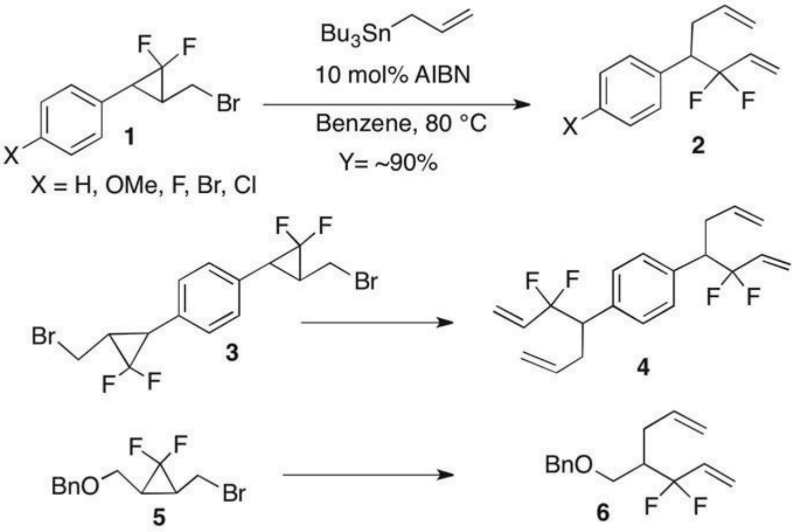

*Fig.1 Regioselective allylation of gem-difluorocyclopropanes*

A synthetic strategy using a building block which has a gem-difluoromethylene moiety has also been recognized as a very attractive route to accessing gem-difluoromethylene compounds. We have been synthesizing gem-difluorocyclopropane compounds and revealed their unique physical- and biological properties. Hence, we have numerous types of gem-difluorocyclopropanes at hand. It was reported that decomposition of the gem-difluorocyclopropane ring took place easily via a radical intermediate with a certain regioselectivity. Inspired by the results, we attempted to prepare novel gem-difluoromethylene compounds through the radical type allylation with ring opening reaction of the gem-difluorocyclopropane ring.

Here we wish to report the details of successful preparation of gem-difluoromethylene compounds using gem-difluorocyclopropanes through regioselective allylation (Fig. 1).

## P2.4

# Photochemical Properties of the Fluorine Substituted Phosphaalkenes: Quantum Chemical Simulations

**V.I. KHARCHENKO** [(a)(b)*], **L.N. ALEXEIKO** [(b)]

[(a)] Institute of Chemistry, FEB RAS, LABORATORY OF ESQCS - VLADIVOSTOK (RUSSIA)
[(b)] Far Eastern Federal University - VLADIVOSTOK (RUSSIA)

* vikharchenko@gmail.com

The fluorine substituted compounds of low-coordinated phosphorus, including phosphaalkenes (PA) are able to cycloaddition and to form complexes with rare-earth metals, so they are promising molecular systems to create new functional materials for various applications in modern devices of photonics and quantum nonlinear optics [1-3].

In this work the theoretical study of fluorine influence on the photochemical properties, structural and spectral characteristics of the $R^1P{=}CR^2R^3$ ($R^1$, $R^2$, $R^3$ = H, F, $Si(CH_3)_3$, $N(CH_3)_2$) compounds was fulfilled with GAMESS-US Code in the vacuum approximation within density functional theory DFT and TDDFT/PBE0/6-311++G(d,p). On the basis of quantum-chemical calculations within the cluster approximation, the reactivity of fluorine substituted PA was evaluated relatively to the cycloaddition and formation of stable complexes with transition metals.

According to the electronic structure, compositions and energies of the frontier molecular orbitals (MO), spectral characteristics of these compounds, it was proved a presence of strong conjugation of the P=C π-systems in the molecular associates and complexes. The fluorine introducing affects significantly the system polarization and photochemical properties. It was found that P-substitution by the fluorine atom more than C-substitution affects the frontier MOs, the molecule ionization and excitation, that also changes its photochemical activity. The absorption and luminescence spectra of these compounds were shown to depend strongly on the fluorine introducing.

The high polarity of the P=C bond in PA and its strong dependence on the substituent type confirms the need to take into account the solvation effects in quantum chemical simulations of photochemical properties and reactivity of these compounds in solutions.

It is shown that an increase of the steric factor under introducing of bulky substituents, such as, $Si(CH_3)_3$, $N(CH_3)_2$, complicates the dimerization and molecular association processes. According to the calculations, the reaction center to the cycloaddition and complexation with metals is the P=C π-system of PA.

Analysis of electronic structure of the molecular systems in the ground and excited electronic-vibrational states, the process of electron removal, the spectral parameters made it possible to conclude about the possibility of control of photochemical properties of this class compounds by an introduction of substituents with the desired characteristics.

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## P2.5

# New Examples of Radical Addition of Bromodifluoromethyl Containing Reagents to Vinyl Ethers

**<u>I. KONDRATOV</u> [(a)]*, G. POSTERNAK [(b)], N. TOLMACHEVA [(b)], I.I. GERUS [(a)], G. HAUFE [(c)]**

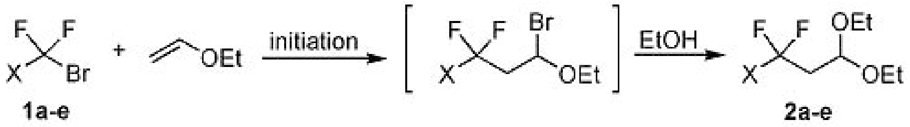
(a) Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)
(b) ENAMINE LTD, CHEMISTRY - KYIV (UKRAINE)
(c) Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)

* Vanya_ko@mail.ru

Radical addition of different polyfluoroalkyl iodides to vinyl ethers was widely investigated and used for the synthesis of various β-polyfluoroalkyl containing acetals and ketals. In contrast there are only few examples in the literature using bromodifluoromethyl containing reagents 1 (X other than Br) in radical addition to vinyl ethers although these reactions would lead to difuoromethylene containing compounds, which are difficult to obtain by other methods. According to the literature data, the radical addition of dibromodifluoromethane (compound 1a, X = Br) to ethyl vinyl ether was studied using different types of initiation [1,2]; among them sodium dithionite ($Na_2S_2O_4$) was found to be the most convenient method.

We applied optimized conditions to carry out hitherto unknown reactions using other bromodifluoromethyl containing reagents 1b-e. In all cases the corresponding products
2b-e were obtained in good yields.

Compounds 2a-e are interesting difluoromethylene containing building blocks. For instance compound 2b was used for the preparation of hitherto unknown 3,3-difluoro-GABA. Other reactions using reagents 1, as well as the chemistry of products 2 will be presented in details.



**a** (X = Br) [1,2]
**b** (X = $CO_2Et$), **c** (X = CN), **d** (X = $PO(OEt)_2$), **e** (X = $SO_2Ph$)

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## P2.6

# Synthesis of New Trifluoromethyl Containing Pyrrolidines

**V. DOLOVANYUK [(a)], I. KONDRATOV [(a)]*, N. TOLMACHEVA [(b)], I.I. GERUS [(a)], G. HAUFE [(c)]**

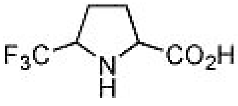
[(a)] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)
[(b)] ENAMINE LTD, CHEMISTRY - KYIV (UKRAINE)
[(c)] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)

* Vanya_ko@mail.ru

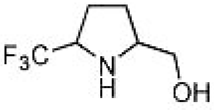
The introduction of a trifluoromethyl group into the α-position of amine fragment attracts attention for medicinal and bioorganic chemistry. A couple of years ago, the $CH(CF_3)NH$-fragment has been proposed as a hydrolytically stable bioisostere of the CONH-group [1]. The $CH(CF_3)NH$-unit can be considered as a group, which combines some properties of the CONH-group (low NH-basicity, $CHCF_3$-NH-CH backbone angle close to 120°, isopolarity of C-$CF_3$ and C=O moieties) and a tetrahedral transition state CH(OH)NH (high electron density on the $CF_3$-group, tetrahedral backbone carbon). On the other hand, the $CH(CF_3)NH$-unit can be considered as amino-group with modified properties owing to the influence of the electronegative and lipophilic $CF_3$-group. Moreover, it has been demonstrated that the introduction of a $CF_3$-group into the α-position of amines improves the oral availability of the compounds and can be used to modify the pharmacokinetic properties [2].

Therefore, the development of synthetic methods towards building blocks containing the $CH(CF_3)NH$-unit is of high interest. In this report we present the synthesis of several pyrrolidines bearing a trifluoromethyl group in α-position, including 5-trifluoromethyl containing analogs of proline 1 [3], prolinol 2 and 2,5-bis(trifluoromethyl)pyrrolidine 3.

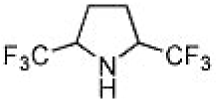
The compounds are interesting as building-blocks. The synthetic pathways and particularities of the chemistry will be presented in detail.



**1**



**2**



**3**

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## P2.7

# New Fluoroalkylation Reactions Involving First Row Metals

**D. VICIC** [(a)]*, **Y. BUDNIKOVA** [(b)], **A. KLEIN** [(c)]

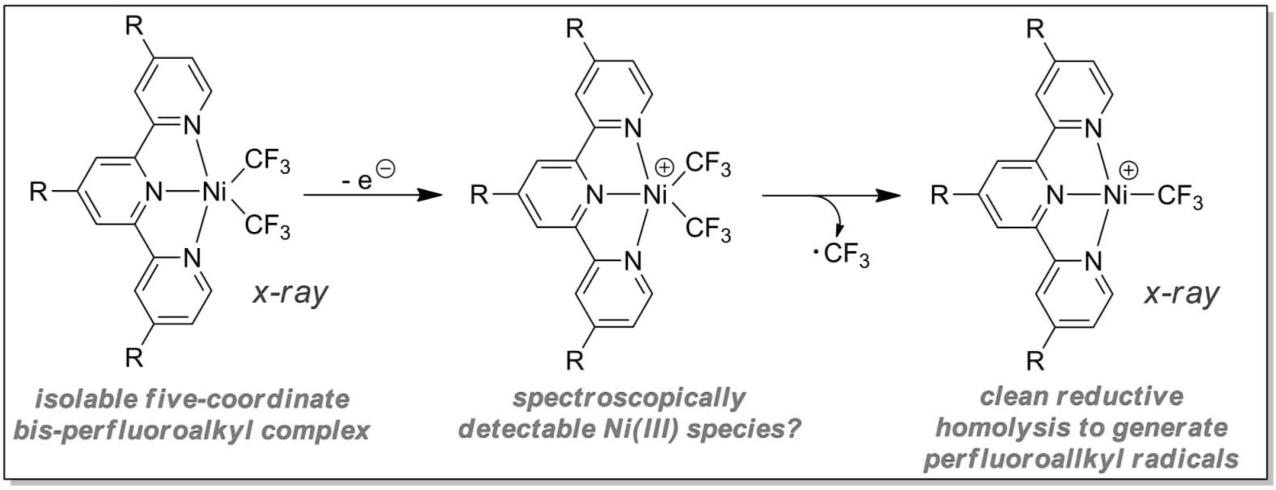
[(a)] LEHIGH UNIVERSITY, DEPARTMENT OF CHEMISTRY - BETHLEHEM (USA)
[(b)] A.E.Arbuzov Institute of Organic and Physical Chem, ELECTROCHEMICAL SYNTHESIS LAB. - KAZAN (RUSSIAN FEDERATION)
[(c)] University of Cologne - COLOGNE (GERMANY)

* dav512@lehigh.edu

In the past ten years, first-row metals have been very successful in mediating the cross-coupling of alkyl electrophiles and alkyl nucleophiles. One of the more successful catalysts for alkyl-alkyl cross-coupling reactions is that based on the nickel/terpyridine system. Here, we present our efforts to understand if such a catalyst system enables the much sought-after perfluoroalkyl cross-coupling reactions. Fundamental studies have been facilitated by the syntheses of new useful nickel precursors which have enabled the study of well-defined nickel perfluoroalkyl complexes. A sample of the complexes and their reactivity is outlined in Scheme 1.

In addition to mediating perfluoroalkyl coupling reactions, inexpensive first-row metals show promise in coupling the $SCF_3$ and $OCF_3$ functionality. Here, we report that nickel-bipyridine complexes were found to be active for the trifluoromethylthiolation of aryl iodides and aryl bromides at room temperature using the convenient $[NMe_4][SCF_3]$ reagent. We also report that well-defined copper and gold complexes have been prepared which contain the first structurally characterized covalent bonds between transition metals and a trifluoromethoxide moiety. The trifluoromethoxide ligand is *O*-bound to both the copper and gold centers, with a copper-oxygen distance of 1.849(4) Å and a gold-oxygen distance of 2.058(4) Å.

**Scheme 1**



## P2.8

# Stereo- and regioselective synthesis of α-fluoroenamides

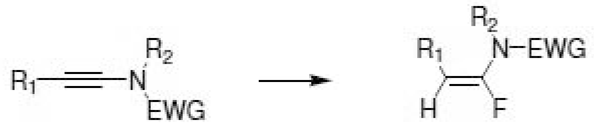
**B. METAYER** [(a)]*, **G. COMPAIN** [(a)], **G. EVANO** [(b)], **A. MARTIN-MINGOT** [(a)], **S. THIBAUDEAU** [(a)]

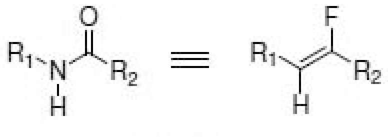
[(a)] Superacid group - Organic Synthesis team - UMR 7285 IC2MP - POITIERS (FRANCE)
[(b)] Laboratoire de chimie organique, Service de chimie et physicochimie organique, Université Libre de Bruxelles - BRUSSELS (BELGIUM)

* benoit.metayer@univ-poitiers.fr

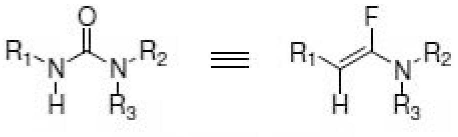
For the last thirty years, the use of fluorinated compounds in medicinal chemistry increased, making the development of new synthetic methodologies to access to nitrogen containing fluorinated compounds a real challenge. Using superacid chemistry, [1] innovative fluorination methods of unsatured nitrogen containing molecules have been developed [2] and recently applied to ynamides. [3]

Starting from functionalized ynamides, the stereo and regioselective hydrofluorination allows accessing to novel (*E*) and (*Z*)-*α*-fluoroenamides. Fluoroolefins are known to be amides' bioisosters, and by analogy, these new fluorinated compounds could be considered as ureido mimetics, with potent applications in medicinal chemistry.





Fluoroolefins :
amides bioisosters



Fluoroenamides :
ureido bioisosters

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## P2.9

# Fluorinated phosphonates, useful synthetic building blocks

**S. OPEKAR** [(a)*], **P. BEIER** [(a)]

[(a)] IOCB, AS CR, ORGANIC SYNTHESIS - PRAGUE (CZECH REPUBLIC)

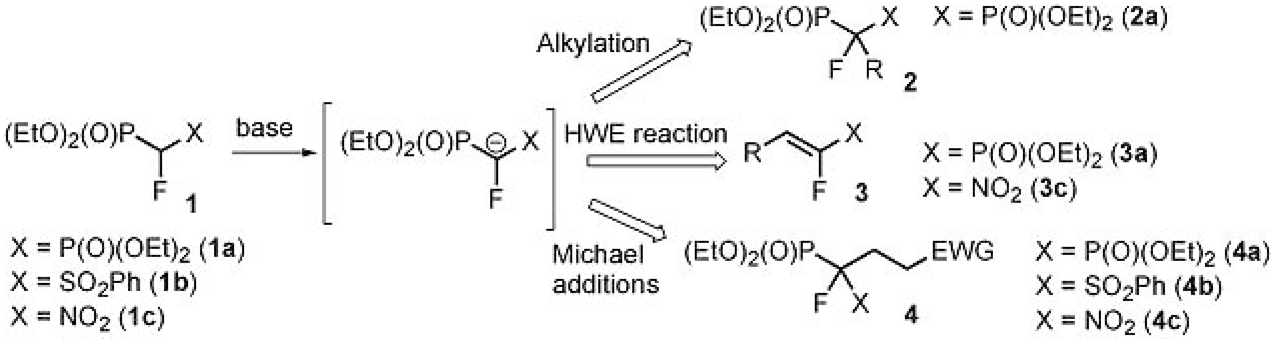
* stanislav.opekar@post.cz

Over the past few decades, phosphonates have emerged as valuable compounds, possessing various biological properties. Their similarity to phosphates is reinforced by the adjunction of fluorine atoms on the carbon linked to the phosphorus [1].

Our research is focused on the utilisation of fluorinated phosphonates in organic synthesis as nucleophilic fluoroalkylation reagents. Fluoromethylphosphonates derivatives (1) can be employed as precursors of potentially biologically active fluorine containing molecules.

Tetraethyl fluoromethylenebisphosphonate (1a) can undergo an alkylation reaction under mild reaction conditions to give alkylated products (2a) [2], Horner-Wadsworth-Emmons reaction with aldehydes to give *geminal* fluorophosphonates olefines (3a) [3] and conjugated addition reactions with activated double bonds to give Michael adducts (4a) [4].

Diethyl fluorophenylsulfonylmethylphosphonate (1b) was subjected to the conjugated addition and Michael adducts (4b) were obtained. Other basic conditions promote unexpected reactions of 1b with a,b-unsaturated ketones.



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## P2.10

# Fluorinated Metal Organic Frameworks : Synthesis and Properties

**E. MAGNIER [(a)]*, C. YU [(a)], H. REN [(a)], T. DEVIC [(a)], P. HORCAJADA [(a)], C. SERRE [(a)], S. BOURRELLY [(b)], P. LLEWELLYN [(b)]**

[(a)] ILV, UMR 8180, BÂTIMENT LAVOISIER, - VERSAILLES (FRANCE)
[(b)] Laboratoire Chimie Provence, MADIREL - MARSEILLE (FRANCE)

* emmanuel.magnier@uvsq.fr

Porous Coordination Polymers (PCPs) or Metal Organic Frameworks (MOFs) are crystalline hybrid solids built up from inorganic units (cluster, chains...) based on transition metals, main group elements or lanthanides connected through organic linkers (poly-carboxylate, -phosphonate, -imidazolate).[1] This defines pores of various shape and size, leading to sometimes very high surface area (above 3000 m2 g-1). Another specific feature of these compounds is that can behave either as rigid (permanent porosity) or flexible (dynamic porosity) compounds. These peculiar behaviors make them promising candidates for various applications in the areas of gas storage (H2, CH4) and capture (CO2), gas or liquids separation, catalysis, controlled drug release and so on.[2] One way for modulating the storage/separation/releasing properties of these hybrid solids is to functionalize the organic component of their walls with groups of variable polarities, acidities influencing the sorption and selectivity processes. Among the possible group, introduction of fluorine atom is promising. Indeed, due to the specific lipophobic and hydrophobic properties of this element, unusual sorption behavior may emerge. This poster will thus presents our results dealing with the synthesis of perfluorinated linkers and their use for the preparation of new MOFs.[3] The properties of these solids, including the evaluation of their hydrophobicity by water sorption experiments, will also be presented.

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## P2.11

# Development of New Reagents for Tetrafluoroethyl and Tetrafluoroethylene Group Transfer

**Y. CHERNYKH** [a]*, **P. BEIER** [b]

[a] IOCB, AS CR - PRAGUE (CZECH REPUBLIC)
[b] IOCB, AS CR, ORGANIC SYNTHESIS - PRAGUE (CZECH REPUBLIC)

* per4eny@gmail.com

A new method for direct introduction of tetrafluoroethyl and tetrafluoroethylene groups has been studied. Compounds $PhSCF_2CF_2Br$ and $PhSCF_2CF_2TMS$ can serve as diradical and radical anion synthons, respectively (Fig. 1) [1-2].

$PhSCF_2CF_2SiMe_3$ undergoes fluoride-initiated nucleophilic addition to electrophilic substrates such as aldehydes, imides and enamines.

A radical $CF_2$ center can be formed by the cleavage of C-S or C-Br bonds under free radical conditions and then added to alkenes or trapped with hydrogen to give $CF_2CF_2H$ moiety.

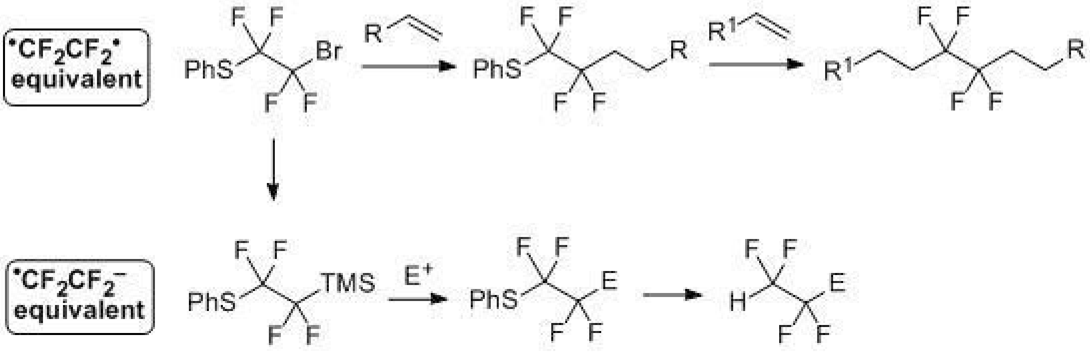

*Fig. 1*

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## P2.12

# Synthesis of Perfluoroalkyl-Substituted γ-Lactones and 4,5-Dihydropyridazin-3(2*H*)-ones via Donor–Acceptor Cyclopropanes

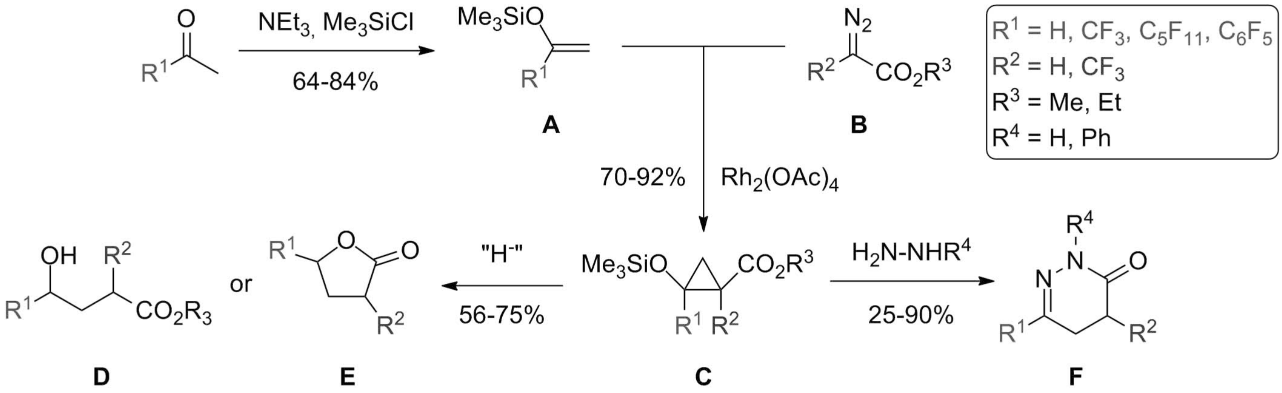
**D. GLADOW** [(a)]*, **H. REISSIG** [(a)]

[(a)] FREIE UNIVERSITÄT BERLIN, INSTITUT FÜR CHEMIE UND BIOCHEMIE - BERLIN (GERMANY)

* Daniel.Gladow@Chemie.FU-Berlin.de

With its high electronegativity and lipophilicity, the introduction of fluorine into organic molecules significantly alters their chemical, physical and biological properties.[1] However, the direct and selective introduction of fluorous groups is still challenging. On the other hand, vicinally donor–acceptor-substituted cyclopropanes serve as masked γ-oxo esters in many synthetically valuable transformations.[2]

The $Rh_2(OAc)_4$-catalyzed decomposition of diazo esters B in the presence of silyl enol ethers A smoothly provided perfluoroalkylated siloxycyclopropanecarboxylates C in good yields. The equivalency of C with γ-oxo esters could be demonstrated by subsequent one-pot transformations yielding perfluoroalkyl-substituted heterocycles. For example, a reduction procedure selectively afforded perfluoroalkyl-substituted γ-hydroxy esters D or γ-lactones E. The condensation with hydrazine or phenylhydrazine delivered a set of perfluoroalkylated 4,5-dihydropyridazin-3(2*H*)ones F.[3]



$R^1$ = H, $CF_3$, $C_5F_{11}$, $C_6F_5$
$R^2$ = H, $CF_3$
$R^3$ = Me, Et
$R^4$ = H, Ph

*Figure 1: Perfluoroalkylated donor–acceptor cyclopropanes serve as masked γ-oxo esters.*

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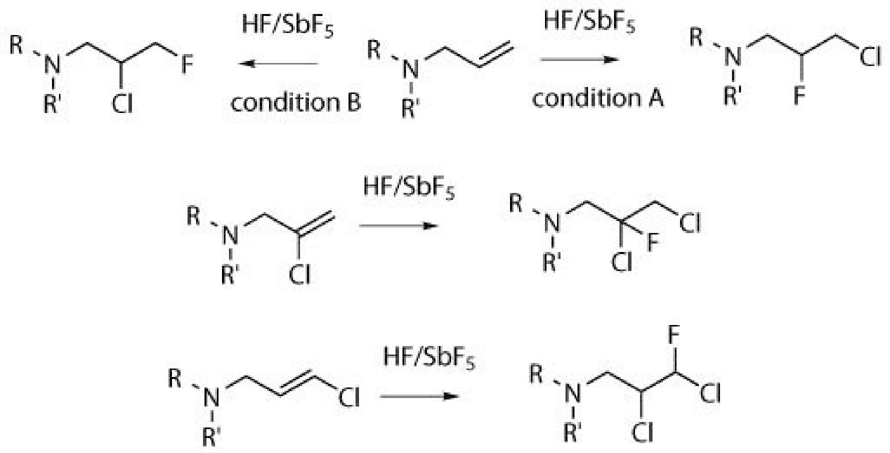
## P2.13

# Haloflurorination reaction in superacid: Acces to new fluorinated nitrogen containing building blocks

**A. LE DARZ** [(a)*], **A. MARTIN-MINGOT** [(b)], **F. BOUAZZA** [(a)], **F. ZUNINO** [(a)], **O. KARAM** [(a)], **S. THIBAUDEAU** [(b)]

[(a)] SARL @rtMolecule, ORGANIC SYNTHESIS TEAM UMR 7285 IC2MP - POITIERS (FRANCE)
[(b)] Superacid group - Organic Synthesis team - UMR 7285 IC2MP - POITIERS (FRANCE)

* alexandre.le.darz@univ-poitiers.fr



Fluorine chemistry is an expanding area of research that is attracting international interest, due to the impact of fluorine in drug discovery. As a consequence, innovative methods to deliver novel fluorinated building blocks are of great interest. In this context, in superacidic conditions,[1] following our recent research work on the synthesis of fluorinated compounds,[2] a halofluorination reaction on unsaturated nitrogen containing compounds was developed. A focus on the mechanism, involving halonium-carbenium superelectrophiles,[3] allowed us to find out reaction conditions to selectively access to new chlorofluorinated building blocks.[4]

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## P2.14

# Fluorocyclization of unsaturated carboxylic acids and alkenols with F-TEDA-$BF_4$ in ionic liquids

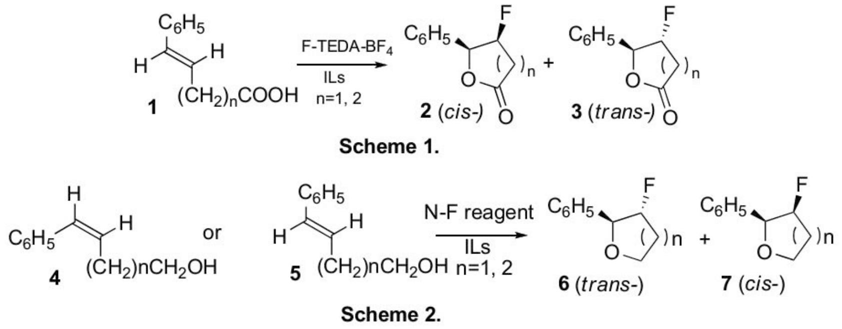
**Y.A. SERGUCHEV [a], L.F. LOURIE [a], M.V. PONOMARENKO [b]*, E.B. RUSANOV [a], M.V. VOVK [a], N.V. IGNAT'EV [c]**

[a] Institute of Organic Chemistry, NAS of Ukraine - KIEV (UKRAINE)
[b] JACOBS UNIVERSITY BREMEN GGMBH, SCHOOL OF ENGINEERING AND SCIENCE - BREMEN (GERMANY)
[c] Merck KGaA, PM-ABE - DARMSTADT (GERMANY)

* maxponom@yahoo.co.uk

Tetrahydrofuran, tetrahydropyran and lactone rings are the key structural units in the natural products like polyether antibiotics, acetogenis, C-glycosides and carbohydrates.

Here we are presenting the results dealing with the application of ionic liquids (ILs) as a reaction media for cyclization reactions of alkenoic acids and alkenols induced by N-F electrophilic reagents.



*Scheme 1, Scheme 2*

The fluorolactonization of unsaturated carboxylic acids 1 under action of the electrophilic reagent F-TEDA-$BF_4$ in an ionic liquid medium provides better stereoselectivity in the formation of the *trans*-isomers 3 in comparison to the reaction in acetonitrile (Scheme 1) [1].

The fluorocyclization of alkenols 4 and 5 under action of N-F reagents (F-TEDA-$BF_4$ and NFSI) in ILs and organic solvents results in the formation of diastereomeric mixture of fluorinated tetrahydropyrans and tetrahydrofurans (Scheme 2) [2]. The fluorocyclization of alkenols 5 in ionic liquids at elevated temperature leads to the formation preferably the *trans*-diastereomeric products 6. This reaction in organic solvents (nitromethane, nitroethane, acetonitrile) is non-selective.

The fluorocyclizations of alkenols and unsaturated carboxylic acids with terminal double bond in ILs as reaction media and nitromethane will be also presented and discussed.

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[2] L.F. Lourie, Y.A. Serguchev, M.V. Ponomarenko, E.B. Rusanov, M.V. Vovk, N.V. Ignat'ev, *Tetrahedron* 69 (2013) 833-838.

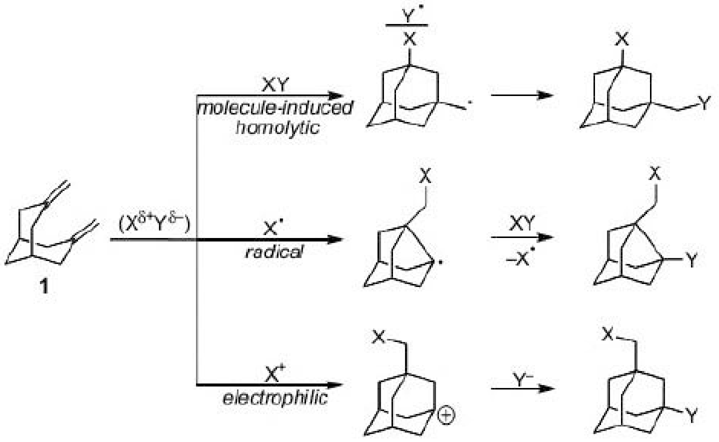
## P2.15

# $F_2$ Reaction with Transannulated Dienes: Regioselectivity and Mechanism

**M.V. PONOMARENKO** [(a)]*, **Y.A. SERGUCHEV** [(b)], **M.E. HIRSCHBERG** [(c)], **G.V. ROESCHENTHALER** [(a)], **A.A. FOKIN** [(d)]

[(a)] JACOBS UNIVERSITY BREMEN GGMBH, SCHOOL OF ENGINEERING AND SCIENCE - BREMEN (GERMANY)
[(b)] Institute of Organic Chemistry, NAS of Ukraine - KIEV (UKRAINE)
[(c)] Inorganic Chemistry, Bergische Universität Wuppertal - WUPPERTAL (GERMANY)
[(d)] Department of Organic Chemistry, Kiev Polytechnic Institute - KIEV (UKRAINE)

* maxponom@yahoo.co.uk



The preparations of the fluorine-containing organic compounds for medicinal, polymer, and material applications usually utilizes a large variety of fluorinating agents rather than direct fluorinations with $F_2$. Exponentially growing attention to direct fluorinations of unsaturated systems is associated with the development of the new electronic materials, e.g., fullerenes, nanotubes and, especially, graphene. However, the addition of fluorine to unsaturated systems mechanistically is not well understood due to discrepancies between the theoretical and experimental data for studied systems [1], as well as formation of the structurally identical fluorinated products by equally feasible mechanisms [2], and spontaneous reactivity of $F_2$ with the studied olefins [3].

Herein we present a combined experimental and computational study of the reaction of $F_2$ with dienes of bicyclo[3.3.1]nonane series that allows to distinct between the free radical, molecule-induced homolytic, and electrophilic addition modes based on the product structure.

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## P2.16

# Fluorine Chemistry on the Postal Stamps

**P. FEDOROV** [(a)]*, **E. CHERNOVA** [(b)]

[(a)] A.M. PROKHOROV GENERAL PHYSICS INSTITUTE RUSSIAN ACADEMY OF SCIENCES, LASER MATERIALS AND TECHNOLOGY RESEARCH CENTER - MOSCOW (RUSSIA)
[(b)] GPI RAS - MOSCOW (RUSSIA)

* ppfedorov@yandex.ru

Many countries put fluorine-related images on their postal stamps. Thus, Mexico placed the symbol of fluorite – one of their exported items – there, and France stamp contains an image of $CaF_2$ cubic crystals – a very important IR optical material and the source for the preparation of HF. Brazil dedicated their stamps to the fluoridation of drinking water. Portraits of scholars who have studied fluorine chemistry can be found on postal stamps, too. Among them Georgius Agricola (1494-1555), who described the application of fluorite as a flux in metallurgy in his *De Re Metallica*; Joens Jacob Berzelius (1779-1848), who discovered hydrofluoric acid and, perhaps, prepared the first nanoparticles of alkaline earth metal fluorides by precipitating them from aqueous solutions; Henri Moissan (1852-1907), who was the first to prepare elemental fluorine by electrolysis, who wrote the first book about fluorine *Le Fluor et ses Composes*, and received the 1906 Nobel Prize in chemistry; and Alexander P. Borodin (1833-1887), Russian doctor, chemist and composer, who was commemorated on a postal stamp unfortunately only as a composer. In his experiments, Borodin proved the monobasicity of HF. He did not obtain elemental fluorine, but was able to show its chemical similarity to chlorine. Borodin also prepared the first man-made organofluorine compound by nucleophilic replacement of chlorine in benzoyl chloride, a technique that is still in use today.

## P2.17

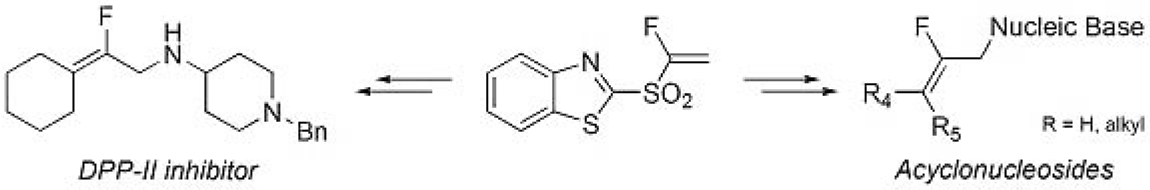
# Application of Modified Julia Reaction for the straighforward preparation of a DPP-II inhibitor and Fluorovinylic Acyclonucleosides

**A. PRUNIER** [(a)]*, **E. PFUND** [(b)], **J. LEGROS** [(c)], **J. MADDALUNO** [(c)], **T. LEQUEUX** [(b)]
[(a)] ENSICAEN, LABORATOIRE DE CHIMIE MOLéCULAIRE ET THIO-ORGANIQUE - CAEN (FRNACE)
[(b)] LCMT - University of Caen - CAEN (FRANCE)
[(c)] IRCOF - MONT-SAINT-AIGNAN (FRANCE)
* anais.prunier@ensicaen.fr

It is well established that the fluorovinylic moiety plays an important role in the field of medicinal chemistry. It has already been introduced onto several compounds to improve their physiological stabilities or their biological activities. The fluorinated carbon-carbon double bond can be used as mimic of the amide bond, preventing the rapid izomerization between both cisoid and transoid forms.[1] The objective is to access to molecules which increased activity, such as Dipeptidyl Peptidase inhibitor II (DPP-II) or acyclonucleosides analogues containing the fluoroalkene motif as potential inhibitors of nucleoside phosphorylases.[2] However, access to highly functionalized fluoroallylamines is not straightforward and required numerous steps.[3] As an alternative our group developed a new strategy based on the modified Julia fluoroolefination using benzothiazolylfluoroaminosulfones derived from piperidine and nucleic bases. Such aminosulfones were prepared by 1,4-conjugated additions of amines or nucleic bases onto fluorovinylsulfones and will be presented (Scheme 1).[4]

Acknowledgement

The European Community (INTERREG IVa channel programme, IS:CE-Chem, project 4061) is thanked for financial support.
*ISCE-Chem* has been selected within the scope of the INTERREG IV A France (Channel) – England cross-border European cooperation programme, co-financed by the ERDF.



*Schema 1: Straightforward synthesis of fluoroallylamines*

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[1] Allmendinger, T.; Felder, E.; Hungerbühler, E. *Tetrahedron Lett.* **1990**, *31*, 7301-7304.
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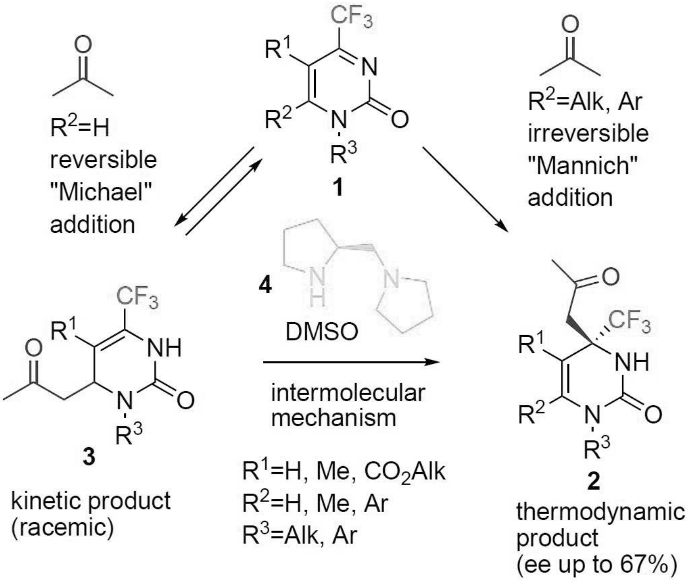
## P2.18

# Thermodynamic and kinetic control of regio- and enantioselectivity in organocatalytic addition of acetone to 4-trifluoromethylpyrimidin-2(1H)-ones

**M.V. VOVK** [a]*, **V. SUKACH** [a], **V. TKACHUK** [a], **V. SHOBA** [a]
[a] Institute of organic chemistry, NAS of Ukraine - KYIV (UKRAINE)
* mvovk@ioch.kiev.ua

It is well known that pyrimidines are very important and highly practicable bioactive compounds. Recently we have described the synthesis of new $CF_3$-containing pyrimidine systems 1. The presence of activated C=N double bond makes possible to modify these compounds by Mannich reaction. In the course of reactivity investigation of 4-trifluoromethylpyrimidin-2(1H)-ones 1 their reaction with acetone in the presence of different amine organocatalysts was examined. It was found that 6-unsubstituted ($R^2$=H) compounds add acetone either at 4th or 6th positions according to thermodynamic or kinetic control. When the reaction was carried out at 25˚C Mannich-like adittion took place (compounds 2). Lower temperature (10-11˚C) led to Michael addition and formation of products 3, which completely rearranged into compounds 2 after warming of the reaction mixture to room temperature. Chiral organocatalyst 4 afforded pure products 2 with enantioselectivity up to 67%.



## P2.19

# Straightforward synthesis of polysubstituted aromatic sulfides by Diels-Alder reactions of perfluoroketene dithioacetals with 1,3-dienes

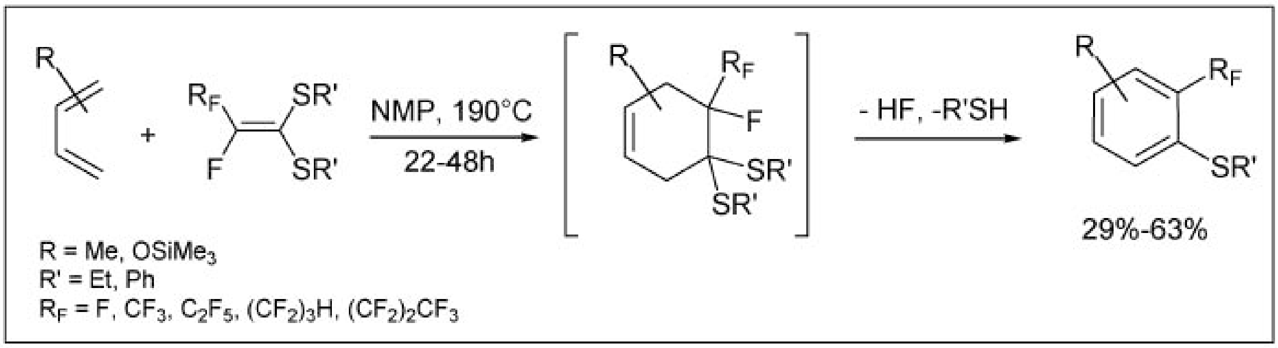
**J.P. BOUILLON** [(a)]*, **S. MIKHAYLYCHENKO** [(a)(b)], **G. DUPAS** [(a)], **Y.G. SHERMOLOVICH** [(a)(b)]

[(a)] UNIVERSITÉ ET INSA DE ROUEN, UMR CNRS 6014 COBRA, IRCOF - MONT SAINT AIGNAN (FRANCE)
[(b)] INSTITUTE OF ORGANIC CHEMISTRY - KYIV (UKRAINE)

* jean-philippe.bouillon@univ-rouen.fr

The Diels-Alder reaction is one of the most powerful synthetic tools in modern organic chemistry. The use of electron-deficient polyfluoroolefins in Diels-Alder reactions affords new types of alicyclic fluorinated compounds. Perfluoroketene dithioacetals are one of the types of fluorine-containing olefins. The use of perfluoroketene dithioacetals in [4+2] cycloaddition reactions with 1,3-dienes has not yet been studied, although Viehe has shown the ability of such compounds to participate in [2+2] cycloaddition reactions.

The poster describes the Diels-Alder reactions of perfluoroketene dithioacetals with electron-rich 1,3-dienes followed by spontaneous HF and thiol elimination, leading to polysubstituted aromatic sulfides in moderate to good yields. Reactions seem to be dependent on the substitution patterns of perfluoroketene dithioacetals. Theoretical calculations performed at the DFT level are in good agreement with the experimental results and show that the overall process is controlled by the cycloaddition step.



R = Me, $OSiMe_3$
R' = Et, Ph
$R_F$ = F, $CF_3$, $C_2F_5$, $(CF_2)_3H$, $(CF_2)_2CF_3$

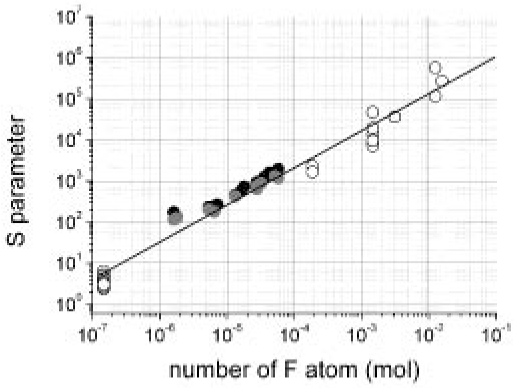
## P2.20

# Absolute method for the quantification of fluorinated molecules using Fluorine liquid NMR covering six decades of concentration – application to Perfluorosulfonic acid (PFSA) ionomer

**C. BAS** [(a)]*, **A. EL KADDOURI** [(a)], **L. FLANDIN** [(a)]

[(a)] LEPMI - UNIVERSITE DE SAVOIE, UMR 5279 - LE BOURGET-DU-LAC (FRANCE)

* corine.bas@univ-savoie.fr



*S parameter from $^{19}$F NMR for small molecules (open symbol) and ionomers (close symbol)*

Fluorine-19 nuclear magnetic resonance in water is commonly employed to detect Perfluorosulfonic acid (PFSA) ionomer [1] or PFSA degradation products [2]. These fluorinated products remain however very diluted in these conditions and challenging to quantify. Interesting attempts have been proposed to quantify PFSA ionomer in water solution by $^{19}$F NMR peak integration, with the help of an external reference [3]. This method appears to be not absolute because of the aggregation phenomenon of PFSA molecules. We propose here that the signal to noise ratio allows a reasonable quantification of the fluorine atom within the solutions (Figure 1) with no use of external or internal reference. This calibration curve was validated for both small molecules as trifluoroacetic acid… and ionomers as Nafion® regardless of their aggregation state. The method exhibits a high sensitivity, and could be directly applied for at least six decades in fluorine atom content in the NMR tube without external reference.

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## P2.21

# Synthesis of new fluorinated cyclic scaffolds

**T. MILCENT [(a)]*, M. KEITA [(b)], S. ONGERI [(b)], B. CROUSSE [(a)]**

[(a)] Faculté de Pharmacie Université Paris Sud, BIOCIS MOLECULES FLUORÉES ET CHIMIE MÉDICINALE - CHÂTENAY-MALABRY (FRANCE)

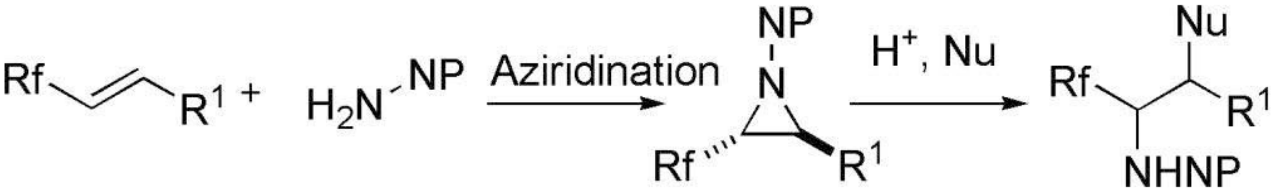
[(b)] UNIVERSITÉ PARIS SUD, MOLÉCULES FLUORÉES ET CHIMIE MÉDICINALE, UMR CNRS 8076, LABEX LERMIT - CHÂTENAY-MALABRY (FRANCE)

* thierry.milcent@u-psud.fr

The synthesis of aziridines has attracted important attention because of their use as central precursors in the preparation of various compounds such as α and β-amino acids, amino alcohols, β-lactam.[1] However, the *N*-amino analogues of aziridines have been less studied whereas they are synthetic precursors of α and β-hydrazino acids. Furthermore, they can be considered as constrained analogues of those hydrazino acid structures, which have a growing interest in the synthesis of peptidomimetics with particular structural and biological properties.[2]

As part of our continuing interest on the synthesis of fluorinated compounds and in particular the access to original fluorinated peptidomimetic units, we focused our attention on the synthesis of fluorinated *N*-aminoaziridines. Indeed these units combine the unique physical and biological properties of fluorine (steric and electronic constraints, increase of the oxidative and proteolytic stability)[3] and the structural characteristics of the three member ring heterocycles. Finally, to our knowledge there is no precedent on the synthesis and reactivity of fluorinated N-aminoaziridines.

A serie of fluorinated *N*-aminoaziridines have been synthesized by the PhI(OAc)$_2$ mediated aziridination procedure. The reaction was carried out with various protected hydrazides and fluorinated alkenes. The reaction was extended to alkenes bearing an amino acids and the ring opening of the CF3-N-aminoaziridines has been investigated.



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## P2.22

# Stereoelectronic Effects in 2-Ammonioethan-1-ides: Experimental and Theoretical Analyses

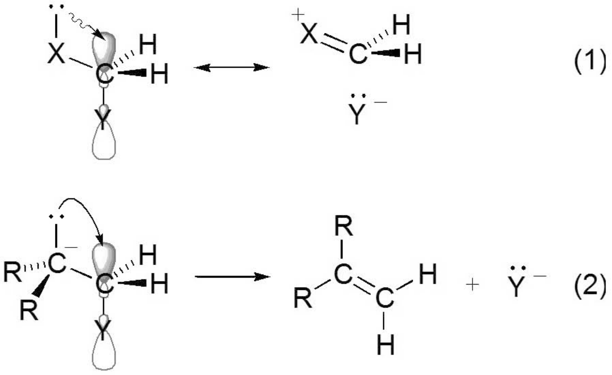
**H. YANAI** [(a)]*, **Y. TAKAHASHI** [(a)], **H. FUKAYA** [(a)], **Y. DOBASHI** [(a)]

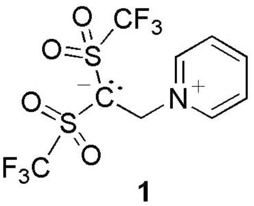
[(a)] TOKYO UNIVERSITY OF PHARMACY AND LIFE SCIENCES, SCHOOL OF PHARMACY - TOKYO (JAPAN)

* yanai@toyaku.ac.jp

The stereoelectronic effect is one of the fundamental concepts in modern organic chemistry. Generally, in the “X–C–Y” system, the negative hyperconjugation of lone pair ($n_X$) on the X atom to the antibonding orbital ($\sigma^*_{C-Y}$) in the C–Y part plays a crucial role to stabilize the conformation (Eqn. 1). Although a number of theoretical studies have also demonstrated that anionic carbon bearing lone pair performs as a good donor for this orbital interaction, there are few experimental works because these species usually bring about fragmentation reaction (Eqn. 2). For instance, dehydration reaction of beta-hydroxycarbonyls via E1cb mechanism and the fragmentation reaction of beta-halogenated ether with zinc, so-called as the Boord reaction, are used as classical reactions to construct carbon–carbon double bond.

Recently we found that zwitterion 1 containing carbanion part and pyridinium part in the molecular structure was obtained in good yield by the reaction of $Tf_2CH_2$, paraformaldehyde, and pyridine. This compound is a stable and nonhygroscopic crystalline compound. An X-ray crystallographic analysis of 1 also confirmed its zwitterionic nature in solid phase. In this analysis, the C1–C2 bond length (149.5 pm) was somewhat shortened, at the same time, the C2–N bond length (151.6 pm) was elongated. Furthermore, the theoretical analysis of this molecule revealed the negative hyperconjugation (the $n_C/\sigma^*_{C-N}$ interaction) in the ‘$C^-$–C–$N^+$’ system. Details will be presented.





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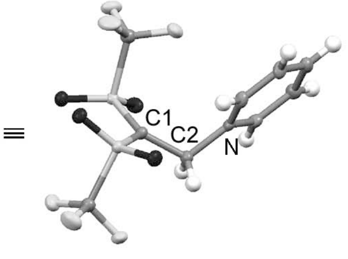


X-ray structure

**P2.23**

# Selective Fluorination of Isoxazoles

**K. SATO** [(a)*], **A. TARUI** [(a)], **M. OMOTE** [(a)], **A. ANDO** [(a)], **G. SANDFORD** [(b)]

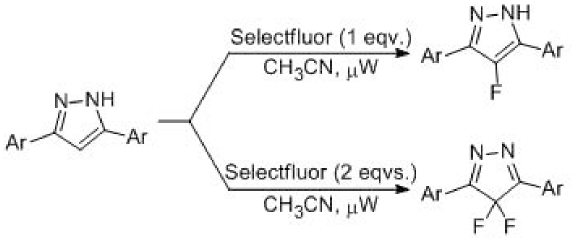
[(a)] FACULTY OF PHARMACEUTICAL SCIENCES, SETSUNAN UNIVERSITY, LABORATORY OF PHARMACEUTICAL CHEMISTRY - HIRAKATA (JAPAN)

[(b)] Department of Chemistry, Durham University - DURHAM (UK)

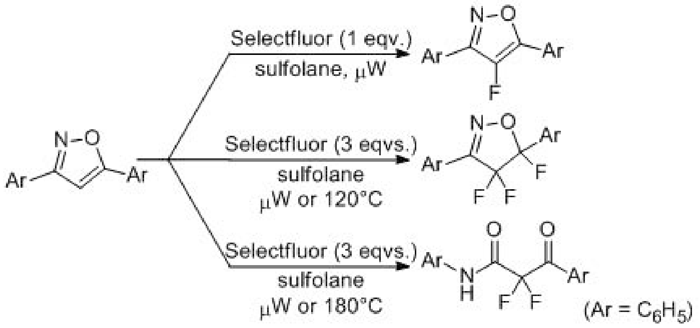
* sato@pharm.setsunan.ac.jp

There is a continuing requirement for the development of efficient and environmentally benign routes for the synthesis of novel fluorinated aromatic and heterocyclic systems for incorporation into life science discovery programmes, because many fluorinated pharmaceutical and agrochemical substances contain fluoro-aromatic or heterocyclic moieties. For example, many fluorinated 6-membered heteroaromatic derivatives find applications in a wide variety of drugs and plant protective materials and, consequently, there are several examples of the synthesis of fluorinated 6-membered heteroaromatic rings by selective fluorination such as pyridine, quinoline and coumarin systems.

Scheme 1.



Scheme 2.



On the other hand, the direct fluorination of 5-membered heteroaromatic systems are rare, although some groups reported the direct fluorination of pyrroles, furans and thiophenes. Furthermore, there are only a few reports of 5-membered heteroaromatic systems that have two heteroatoms such as pyrazoles, isoxaoles and thiazoles.[1–3]

We recently reported the selective fluorination of pyrazoles with Selectfluor™, to give mono-fluorinated or di-fluorinated pyrazoles in moderate to good yields (Scheme 1).[4] In the expansion of this reaction, we would like to report selective fluorination of isoxazoles and the newest results (Scheme 2).

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## P2.24

# The Activation of Sulfur Hexafluoride at Low-Coordinate Nickel Dinitrogen Complexes

**P. HOLZE** [(a)]*, **C. LIMBERG** [(b)]

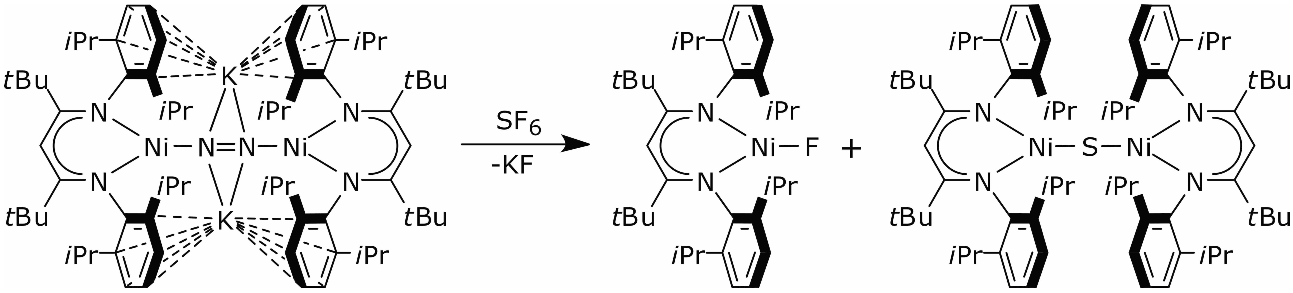
[(a)] Humboldt-Universität zu Berlin, AK Limberg - BERLIN (GERMANY)
[(b)] Humboldt-Universität zu Berlin - BERLIN (GERMANY)

* patrick.holze@chemie.hu-berlin.de

Sulfur hexafluoride is widely regarded as an extremely inert molecular gas. Due to its vast stability towards both nucleophilic and electrophilic attack, reports on its successful chemical activation are scarce. Only Ernst *et al.* described the conversion of $SF_6$ using transition metal complexes. Mostly, these led to mixtures of different metal fluoride complexes but no sulfur containing metal complex was isolated.[1-2]

In previous studies of our group, highly reduced low-coordinate *β*-diketiminato nickel complexes bearing a labile co-ligand were applied to the activation of small molecules. For instance dinitrogen, dihydrogen and carbon monoxide, but also elemental sulfur and phosphorus were activated and/or derivatised.[3-7] Herein, we show that even the rather inert $SF_6$ molecule can be converted under standard conditions.

The reaction of a reduced, low-coordinate nickel dinitrogen complex leads to a nickel(II)-sulfide and a nickel(II)-fluoride complex. The reaction was monitored by paramagnetic $^1$H NMR, IR and EPR spectroscopy giving insight into the mechanism of the eight-electron reduction of $SF_6$.



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## P2.25

# Synthesis of 2-Aryl-3-trifluoromethylquinolines using (*E*)-Trimethyl(3,3,3-trifluoroprop-1-enyl)silane

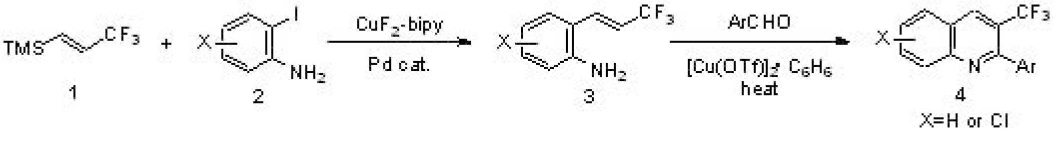
**M. OMOTE** [(a)]*, **M. TANAKA** [(b)], **M. TANAKA** [(b)], **A. IKEDA** [(a)], **A. TARUI** [(a)], **K. SATO** [(a)], **A. ANDO** [(a)]

[(a)] FACULTY OF PHARMACEUTICAL SCIENCES, SETSUNAN UNIVERSITY, LABORATORY OF PHARMACEUTICAL CHEMISTRY - HIRAKATA (JAPAN)
[(b)] FACULTY OF PHARMACEUTICAL SCIENCES, SETSUNAN UNIVE - HIRAKATA (JAPAN)

* omote@pharm.setsunan.ac.jp

Trifluoromethylated quinolines have recently been the subject of considerable levels of attention because of the important roles they play in pharmaceutical, agrochemical and high-performance materials. A wide variety of synthetic methods have been reported for the construction of 2- and 4-trifluoromethylquinolines. In contrast, synthetic studies towards the development of methods providing access to 3-trifluoromethylquinolines remain scarce. The main difficulty associated with the construction of the 3-trifluoromethylquinoline core is the lack of a useful synthetic protocol that is compatible with the use of common aniline derivatives. Particularly, the synthesis of 2-substituted-3-trifluoromethylquinolines becomes incredibly difficult because of the steric hindrance provided by the trifluoromethyl group. The difficulties associated with the construction of 3-trifluoromethylquinolines have limited their use in the synthesis of several promising therapeutic targets. With these issues in mind, we envisaged that the development of an efficient synthetic protocol involving the use of aniline derivatives would provide facile access to a wide range of 2-substituted-3-trifluoromethylquinolines, and complement the existing library of trifluoromethylquinolines already available for the synthesis of potential therapeutic agents.

We recently reported the use of (*E*)-trimethyl(3,3,3-trifluoroprop-1-enyl)silane (1) for the 3,3,3-trifluoropropenylation of aryl iodide according to the Hiyama cross-coupling reaction to afford β-trifluoromethylstyrene derivatives, demonstrating that 1 was a useful 3,3,3-trifluoropropenylation reagent for aryl iodides. During the course of that particular study, the Hiyama cross-coupling reaction of 1 was found to be applicable to 2-iodoaniline (2) when the reaction was conducted in the presence of copper(II) fluoride coordinated by 2,2’-bipyridine (bipy), affording key intermediate 3. The structure of 3 was critical to the success of the subsequent oxidative cyclocondensation reaction because the 3,3,3-trifluoroprop-1-enyl chain of 3 was perfectly aligned to participate in the cyclocondensation reaction. The oxidative cyclization reaction itself proceeded smoothly in the presence of copper(I) salt to give a series of 2-aryl-3-trifluoromethylquinolines (4). Herein, we wish to report the synthesis of 4 via the Hiyama cross-coupling reaction of 1 with 2 followed by an oxidative cyclocondensation reaction.



## P2.26

# C–F and S–F Activation Reactions at Binuclear Rhodium Hydrido Complexes

**L. ZAMOSTNA** [(a)]*, **M. AHRENS** [(a)], **T. BRAUN** [(a)]

[(a)] Humboldt-Universität zu Berlin, Department of Chemistry - BERLIN (GERMANY)

* lada.zamostna@chemie.hu-berlin.de

C–F bond cleavage reactions can be considered as key steps for the derivatization of highly fluorinated compounds at transition metal centers.[1] Rhodium complexes like [Rh(Bpin)(PEt$_3$)$_3$] and [Rh(H)(PEt$_3$)$_3$] have proved to be efficient in activating C–F bonds often resulting in unique selectivities.[2] Binuclear rhodium hydrido complexes as for instance [Rh($\mu$-H)(dippp)]$_2$ (dippp=bis(diisopropyl-phophino)propane) provide a high reactivity, in part because of their electron-deficient character. Thus, [Rh($\mu$-H)(dippp)]$_2$ reacts with fluoroarenes to give the fluorido complex [Rh($\mu$-F)(dippp)]2 and hydrodefluorinated organic products. Treatment of [Rh($\mu$-F)(dippp)]$_2$ with silanes results in the formation of unique $\eta^2$-silane hydrido complexes. A catalytic hydrodefluorination was developed on using [Rh($\mu$-H)(dippp)]$_2$ as catalytic precursor and HSiEt$_3$ as a hydrogen source.

Moreover, [Rh($\mu$-H)(dippp)]$_2$ has found to be highly reactive towards S–F bonds. (Pentafluorosulfanyl)benzenes and SF$_6$ can be activated resulting in the formation of the fluorido complex [Rh($\mu$-F)(dippp)]$_2$. The reaction with ArSF$_5$ (Ar=Ph, C$_6$H$_4$CH$_3$) leads additionally to binuclear rhodium hydrido thiolato-bridged derivatives. Note that SF$_6$ is a potent greenhouse gas featuring a remarkably high global warming potential. Hence, the deconstruction of S–F bonds can be of great interest to environmental chemistry.[3]

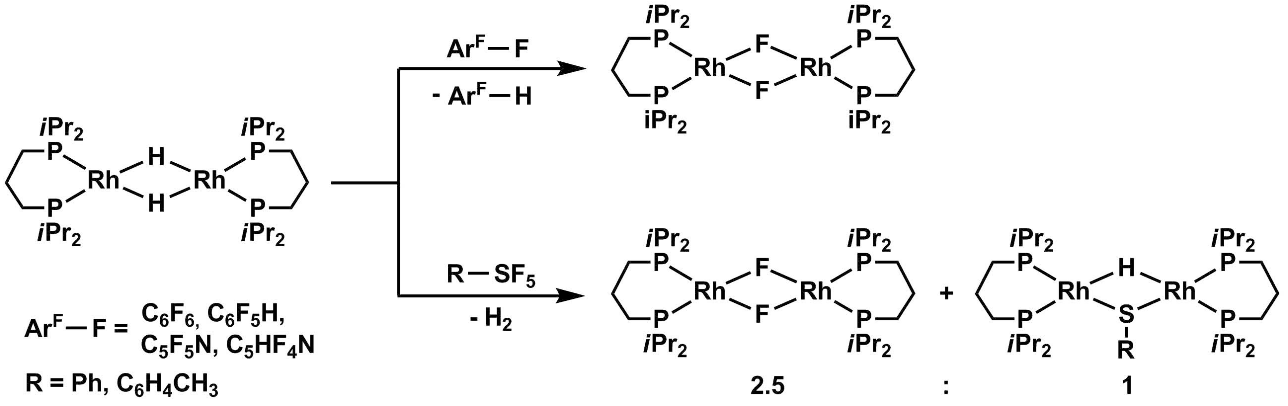


*Fig. 1. C–F and S–F bond activation at a binuclear rhodium hydrido complex*

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## P2.27

# Synthesis, structure, physical and chemical properties and potential applications of fluorinated lignin

**A. TSVETNIKOV [(a)]*, L. MATVEENKO [(a)], Y. NIKOLENKO [(a)], A. USTINOV [(a)], V. KURIAVIY [(a)], D. OPRA , S. SINEBRYUKHOV [(a)], S. GNEDENKOV [(a)]**

[(a)] INSTITUTE OF CHEMISTRY FAR-EAST BRANCH OF THE RUSSIAN ACADEMY OF SCIENCE - VLADIVOSTOK (RUSSIA)

* tsvetnikov@ich.dvo.ru

A necessity to dispose million tons of hydrolyzed lignin (HL) generated as a result of the chemical processing of wood as well as creation of the compact and powerful power supplies are the critical goal of modern age. In the Institute of Chemistry, FEB of RAS, the methods of producing the fluorinated hydrolyzed lignin (FHL) for cathodes of lithium electrochemical power sources were developed that allows to increase several times their storage densities and, thereby, to prolong service life period of self-contained devices. In the course of the thermal destruction of the polytetrafluorethylene waste, a large amount of the gaseous tetrafluoroethylene and hexafluoropropylene is generated which can be used for soft fluorination of HL under certain conditions. In this case, the product containing about 5% of fluorine is derived тора. The fluorination of HL using the high-purity gaseous fluorine diluted with nitrogen allows to increase the fluorination degree to 20-25%. The maximum quantity of fluorine atoms in the lignin composition is reached by the liquid-phase fluorination of HL with bromine trifluoride obtained by way of passing fluorine through the liquid bromine using the fluorine generator Generation-F® 80.

A was studied by XPS. HL consists of macromolecules (molecular mass $10^2$ - $10^6$) without any regular configuration. Structure of HL contains aliphatic and aromatic carbons. Part of carbons is bound with oxygen. The complex spectra C1s and F1s were simulated by computer to analyze the chemical states of carbon and fluorine in the FHL. The broad F1s line of FHL is constructed from two peaks with $E_b$ =689.2±0.2 eV (F1) and $E_b$=687.8±0.2 eV (F2). In accordance with the $E_b$ the line F1 may be assigned to fluorine covalently bound with carbon in the ≡CF and $>CF_2$ groups. The respective lines in the C1s spectra are present with the $E_b$ which equal 290.5±0.2 eV and 292.5±0.2 eV, correspondingly. Binding energy of the F2 allows to refer this line to the fluorine which forms with carbon the semi-ionic bond. Binding energy of respective C1s peak equals 289.2±0.2 eV. The presence of semi-ionic carbon-fluorine bonds is caused by the HL structure containing the aliphatic and aromatic carbons.

Using the methods of impedance spectroscopy, scanning electron microscopy and energy dispersive spectroscopy, the conductivity, morphology and composition of elements of the FHL were studied. The basic parameters and behavior of the lignin-based lithium electrochemical power sources using two electrolyte systems, namely, 1 M $LiBF_4$ in g-butyrolacton and 1 M $LiClO_4$ in propylene carbonate, were investigated. According to data of scanning electron microscopy (SEM), the sizes of particles forming HL vary within the range of 5 to 30 mm while the particle itself has at the surface the extensive network of micro- and macropores. Such porosity and netted morphologic structure of HL can, to a great extent, facilitate the solid-state diffusion of lithium cations within the cathode volume when the lithium power source operates.

## P2.28

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# Self-assembly of amphiphilic semifluorinated block copolymers at interfaces

**O. ZAMYSHLYAYEVA [a]*, N. MELNIKOVA [b], O. LAPTEVA [c], M. BATENKIN [d], Y. SEMCHIKOV [c]**

[a] N.I. Lobachevsky Nizhniy Novgorod State University, DEPARTMENT OF MACROMOLECULAR CHEMISTRY AND COLLOID - NIZHNIY NOVGOROD (RUSSIA)
[b] Nizhny Novgorod State Medical Academy - NIZHNIY NOVGOROD (RUSSIA)
[c] N.I. Lobachevsky Nizhniy Novgorod State University - NIZHNIY NOVGOROD (RUSSIA)
[d] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences - NIZHNIY NOVGOROD (RUSSIA)

* zam.olga@mail.ru

Amphiphilic block copolymers capable of self-assembly at the air-water interface are very attractive materials due to their interesting nanoscopic structures [1]. Particular interests are amphiphilic fluorine-containing polymers, which are capable of self-assembly at the air-water interface. Stability of the resulting structures is a function of solution equilibrium conditions prior to spreading and after evaporation of the spreading solvent. The aim of this work is to study the effect of the solvent nature, the molecular mass of the polymers, solution concentration on spreading conditions of formation of monomolecular films of block copolymers of N-vinylpyrrolidone-block-2,2,3,3-tetrafluoropropylmethacrylate (PVP-*block*-PFMA) at the interface water-air. This block copolymers with different length of the hydrophilic block were obtained by the method described in [2]. Monomolecular layers of the block copolymers were studied by film balance Langmuir-Blodgett KSVmini (Finland) using the Wilhelmy plate. The phenomenon of surface micelle formation for the studied copolymers with different length of the hydrophilic block was discovered. Was defined critical micelle concentration in the surface layer. To block copolymer Mw(PVP)=57000 value of this quantity was 38 ml, for block copolymers with Mw(PVP)=43000 and 22000 - 30 ml. At molecular mass of the hydrophilic block 26000 micelles do not formed. It is shown that stable monolayer formed from chloroform-methanol solutions, and the surface pressure at the point of collapse is defined particle size of the micellar solutions. Analysis of molecular spectra of solutions of block copolymers showed intensive structuring in methanol solutions, caused by hydrophobic interaction of macromolecules of the polymer and solvent molecules [3]. Topography of the surface of the films studied in the unit «Solver Bio NT-MDT» in tapping mode. It was found that in Langmuir-Blodgett films link PFMA segregate to the surface layer, forming hydrophobic surface. The surface free energy of Langmuir-Blodgett films of PVP-*block*-PFMA was determined by wetting.

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## P2.29

# Sonogashira cross-coupling reaction using (*E*) -trimethyl(3,3,3-trifluoroprop-1-enyl)silane and subsequent cyclization to indoles

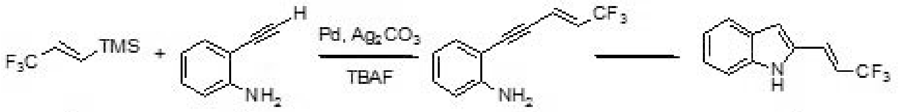
**A. IKEDA** [(a)*], **M. OMOTE** [(a)], **A. TARUI** [(a)], **K. SATO** [(a)], **A. ANDO** [(a)], **Y. SHIRAI** [(a)], **K. KUSUMOTO** [(a)]

[(a)] FACULTY OF PHARMACEUTICAL SCIENCES, SETSUNAN UNIVERSITY, LABORATORY OF PHARMACEUTICAL CHEMISTRY - HIRAKATA (JAPAN)

* 12d401ia@edu.setsunan.ac.jp

The enyne scaffold is present in a number of bioactive or natural products and plays an important role in organic chemistry. Hence, there are many reports on enyne synthesis, involving dehydration of propargyl alcohol, Wittig reaction of propargyl aldehyde and Sonogashira cross-coupling reaction. In particular, Sonogashira cross-coupling reaction has been used frequently for the enyne synthesis and various modifications were realized. However, it is quite difficult to make enyne compounds having $CF_3$ group on the terminal $sp^2$ carbon because there is no sustainable method to construct such a thermally labile structure. Therefore, it is still a challenging task to develop a new synthetic methodology for the trifluoromethylated enynes potentially useful for further transformation as well as intrinsic drug candidates.

Previously, we have prepared (*E*)-trimethyl(3,3,3-trifluoroprop-1-enyl)silane 1 and demonstrated that 1 was an excellent 3,3,3-trifluoropropenylation agent of aryl iodide in Hiyama cross-coupling reaction. During the course of this experiment, we found that 1 could be applicable to Sonogashira cross-coupling reaction to construct the trifluoromethylated enynes and some products could be transformed into indoles through intramolecular cyclization. Indeed, the reaction of 1 with 2 was performed effectively to yield 3 using TBAF as a fluoride anion in the presence of Pd catalyst and $Ag_2CO_3$. Addition of $InBr_3$ into the reaction increased the yield of 3 substantially. Subsequently, cyclization of 3 into indole 4 was carried out with Pd catalyst in moderate yield. Details of the conditions, scope and limitation of this coupling reaction and subsequent cyclization will be discussed.



1 2 3 4

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## P2.30

# The asymmetric synthesis of $CF_3$- or -$CF_2$- substituted tetrahydroquinol-ines by employing chiral phosphoric acid as catalyst

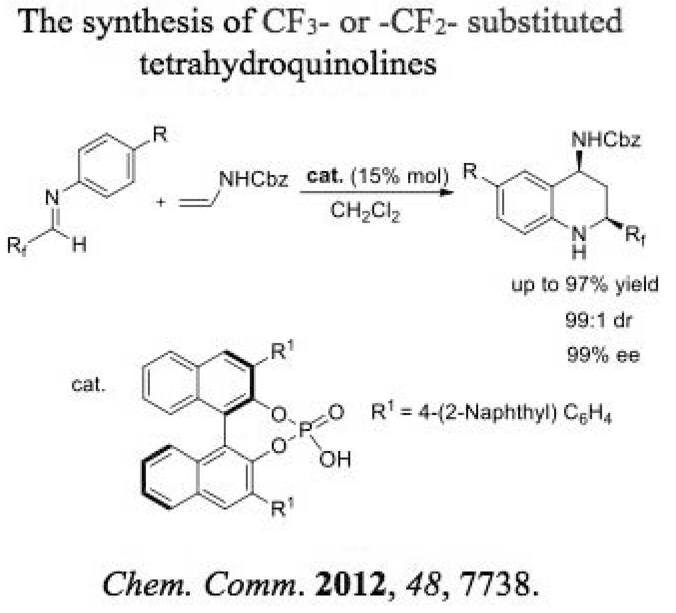
**J.H. LIN** [(a)] , **G. ZONG** [(a)], **Z. ZHOU** [(a)], **R.B. DU** [(a)], **J.C. XIAO** [(a)*], **S. LIU** [(b)]

[(a)] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences - SHANGHAI (CHINA)
[(b)] Research Computing Center, University of North Carolina - CHAPEL HILL (USA)

* jchxiao@gmail.com

Tetrahydroquinoline derivatives always exhibit interesting biological activity.[1] Preparation of these novel compounds continues to be an important goal of synthetic organic chemists. Although the $CF_3$-substituted tetrahydroquinoline derivatives have been previously obtained,[2] the asymmetric synthesis of $CF_3$- or -$CF_2$-substituted tetrahydroquinolines has never been realized.

Chiral BINOL-derived phosphoric acids, as an efficient class of organocatalyst, have been applied in a variety of asymmetric organic synthesis.[3] Combined with the potential importance of $CF_3$- or -$CF_2$-substituted tetrahydroquinolines, we explored their asymmetric synthesis by chiral phosphoric acid catalysis.


The synthesis of $CF_3$- or -$CF_2$- substituted tetrahydroquinolines

*Chem. Comm.* **2012**, *48*, 7738.

*The synthesis of $CF_3$- or -$CF_2$- substituted tetrahydroquinolines*

It was found that $CF_3$- or -$CF_2$- substituted tetrahydroquinolines could be obtained with excellent diaselectivity and enantioselectivity based on the reaction of N-arylimines with benzyl N-vinylcarbamate in the presence of chiral phosphoric acid. The results presented here provide a versatile platform for the asymmetrical synthesis of tetrahydroq-uinoline derivatives with potential interesting bioactivity. Studies to the synthesis of other enantioenriched $CF_3$- or -$CF_2$- group substituted compounds are currently underway.

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## P2.31

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# Photoinduced Copolymerization of Perfluorodiiodide and Cyclohexanediol Diacrylate

**T. YAJIMA** [(a)]*, **M. SHINMEN** [(a)]

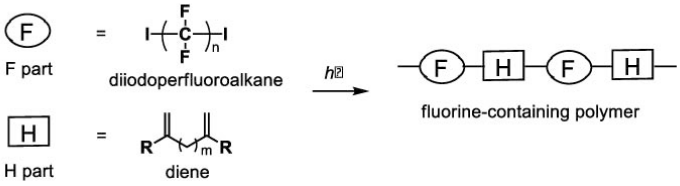
[(a)] Ochanomizu University, CHEMISTRY - TOKYO (JAPAN)

* yajima.tomoko@ocha.ac.jp

Polymers with perfluoroalkyl ($R_f$) group have remarkable and unique properties such as excellent chemical resistance, thermostability, hydrophobicity, non-adhesive properties, low friction coefficients, and antifouling behaviours.

Based on our previous study on photoinduced perfluoroalkylation of electron-deficient olefins [1], we designed the photoinduced polymerization using diene and diiodoperfluoroalkane (Figure 1). We have already reported that the photoinduced polymerization of daicrylate and diiodoperfluoroalkane proceeded smoothly to give copolymer. (Scheme 1)[2]. Here, we develop this synthetic method for the synthesis of chiral polymers using cyclohexenediol diacrylate as a diene.

Figure 1.



Scheme 1.

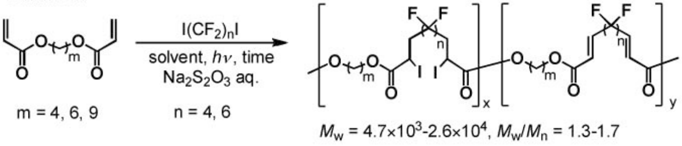
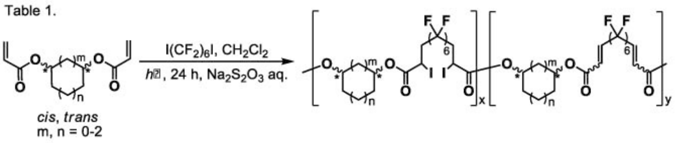


Table 1.



| entry | m | n | *cis, trans* | $M_w$ a) | $M_w/M_n$ a) | x : y b) | x + y b) | yield% c) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 2 | *cis* | $1.3\times10^4$ | 1.2 | 1 : 0.5 | 18.4 | 12 |
| 2 | | | *trans* | $1.2\times10^4$ | 1.4 | 1 : 1.9 | 17.1 | 25 |
| 3 | | | *cis, trans* mix | $1.2\times10^4$ | 1.4 | 1 : 0.3 | 16.9 | 18 |
| 4 | 1 | 1 | *cis, trans* mix | $1.3\times10^4$ | 1.5 | 1 : 1.6 | 21.7 | 52 |
| 5 | 2 | 0 | *cis, trans* mix | $2.7\times10^4$ | 1.5 | 1 : 3.6 | 45.7 | 58 |

a) Determined by GPC. b) Determined by $^1H$ NMR. c) Hexane-insoluble part.

The reaction of cyclohexenediol daicrylate and 1,6-diiodoperfluorohexane was carried out in the presence of aqueous $Na_2S_2O_3$ under UV irradiation in $CH_2Cl_2$. The reaction was proceeded with partial elimination of HI to give the polymer which contains both iodide part and olefinic part (Table 1). The degree of polymerization was influenced by substituent patterns (1,4-substitution > 1,3- > 1,2-).

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## P2.32

# THE INFLUENCE OF FLUORINATION ON THE HYDROGEN BOND DONATING CAPACITY OF ALCOHOL

**G. COMPAIN** [(a)]*, **B. LINCLAU** [(b)]

[(a)] University of Southampton, MOLECULAR DIAGNOSTICS AND THERAPEUTICS SECTION - SOUTHAMPTON (UNITED KINGDOM)
[(b)] University of Southampton - SOUTHAMPTON (UNITED KINGDOM)

* g.compain.gc@gmail.com

The hydrogen bond (H-bond) is an important specific interaction between a molecule and its local environment.[1] Given the strong electrostatic contribution to the overall energy of a H-bond, the introduction of a small and highly electronegative fluorine atom is expected to significantly modify the H-bond properties of an adjacent FG. The strong inductive effect of fluorine is generally considered to lead to an increase in hydrogen bond donating capacity of adjacent functional groups.[2]

We have shown that this is not always the case for fluorohydrins, and that a reduction in hydrogen bond donating capacity is also possible. This reduction was found to be quite significant in some cases.[3]

This presentation will give an overview of the results obtained, with a tentative rationale for the observed effects.

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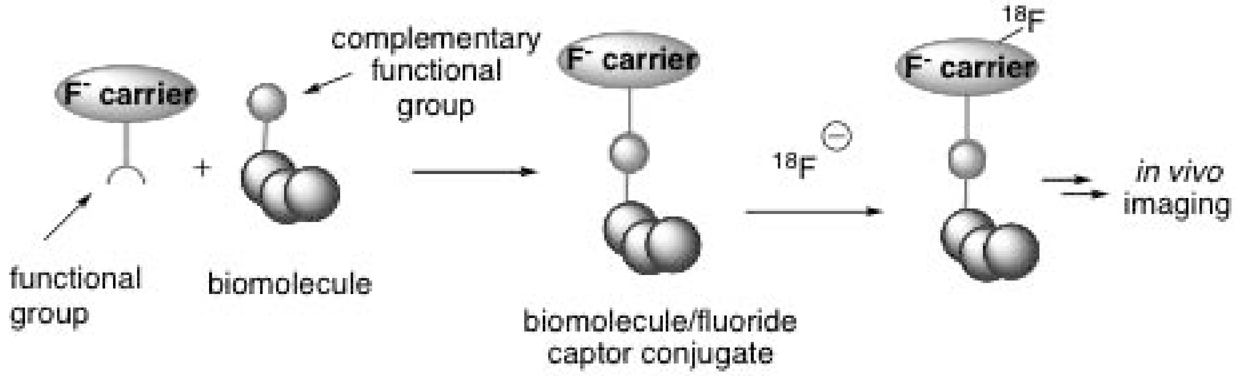
## P2.33

# Recent progress in the development diagnostic tools via radiofluorinated probes.

**E. GRAS** [a]*, **B. MESTRE VOEGTLE** [b], **S. CADET** [a]
[a] LCC - TOULOUSE (FRANCE)
[b] LSPCMIB - TOULOUSE (FRANCE)
* emmanuel.gras@lcc-toulouse.fr

Cationic boranes have proved to be excellent anion sensors capable of forming highly stable adducts with fluoride in water and even transfer the fluoride from an aqueous phase to an organic phase.[1,2]

We are currently developing a process based on the ability of cationic boronic derivatives to form highly stable trifluoroborate zwitterions in the presence of fluorides in buffered solutions at physiological pH.[3] This characteristic is of major interest for radiofluorination purposes. Indeed it has been shown that radiolabeled trifluoroborates can be obtained either from the boronic derivative (acid or ester) or by isotope exchange, both with high specific radioactivities.[4-6] We will present our first results aiming at performing the functionnalization of the boronate and their conjugation to biomolecules.



*Labelling biomolecules with fluorides "made easy"*

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[6] Z. Li, et al. Med. Chem. Commun? 2012, 3, 1305.

## P2.34

# Synthesis of new N-difluoromethyl peptidomimetics derivatives

**M. MAMONE** [(a)]*, **T. MILCENT** [(a)], **B. CROUSSE** [(a)]

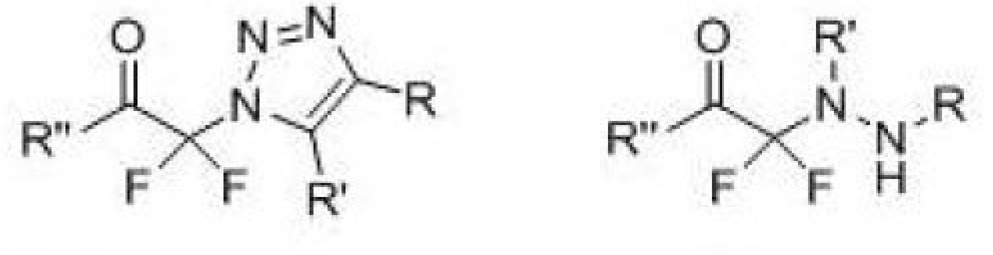
[(a)] Faculté de Pharmacie Université Paris Sud, BIOCIS MOLECULES FLUORÉES ET CHIMIE
MÉDICINALE - CHÂTENAY-MALABRY (FRANCE)

* marius.mamone@u-psud.fr

Due to their specific physico-chemical features (highly hydrophobic, electron rich, sterically demanding), the fluorinated groups can greatly modify the behaviour of a molecule in a biological environment. [1] Indeed, incorporation of fluoroalkyl groups into peptides and peptidomimetics can improve their resistance to metabolism, modify their structural properties and hence their binding with an enzyme or a receptor. [2]

However, only few methods to introduce difluoromethyl moiety directly on a heteroatom are described and these building blocks are scarcely used in a peptidic or peptidomimetic synthesis.

In continuation of our interest in the synthesis of original fluorinated peptidomimetics and in order to study the influence of these groups on the conformation of peptidomimetics, we present the preparation of new hydrazino and triazol N-difluoromethyl derivatives.



*Example of N-diluoromethyled peptidomimetics*

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## P2.35

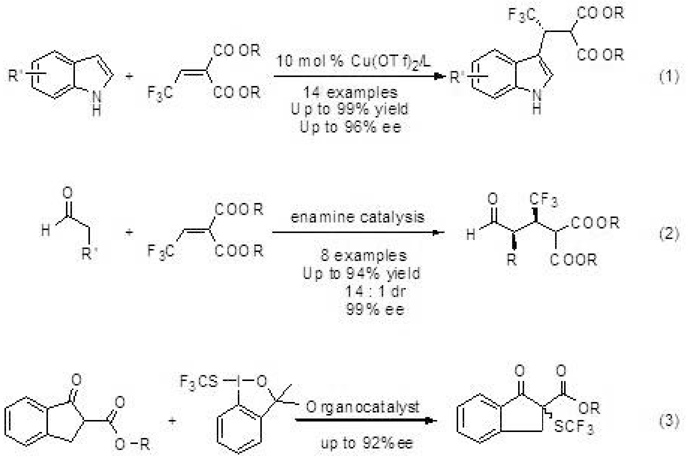
# Catalytic Asymmetric Construction of Chiral Carbon Center with a $CF_3$ or $CF_3S$ Group

**L. LU** [(a)]*

[(a)] Shanghai Institute of Organic Chemistry, Key Laboratory of Organofluorine Chemistry, KEY LABORATORY OF ORGANOFLUORINE CHEMISTRY, CAS - SHANGHAI (CHINA)

* lulong@sioc.ac.cn

The stereospecific incorporation of trifluoromethyl or trifluoromethylthiol group into an organic compounds has attracted considerable attention, mainly due to the incorporation of these groups into organic compounds often leads to enhanced binding selectivity, higher lipophilicity and increased metabolic stability. Although many methodologies for the preparation of optically active fluorinated compounds have been reported, the development of general catalytic methods for the construction of stereogenic carbon center bearing a trifluoromethyl or trifluoromethylthiol group remains not only a demand for biochemists and medicinal chemists, but also a challenge for synthetic organic chemists.



Herein, we present several methods for the asymmetric construction of trifluoromethyl- or trifluoromethylthiol-substituted carbon center with good yields (up to 99%) and good enantiomeric excesses (up to 86% ee). The reactions were tolerant with a broad range of substrate scope.

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[3] Wen, L.; Shen, Q.; Lu, L. *Org. Lett.* **2010**, *12*, 4655-4657.

**P2.36**

# Mechanistic Insights into Generation of $CF_3$ Radicals from Hypervalent Iodine Reagents

**N. SANTSCHI** [(a)*], **A. TOGNI** [(b)]

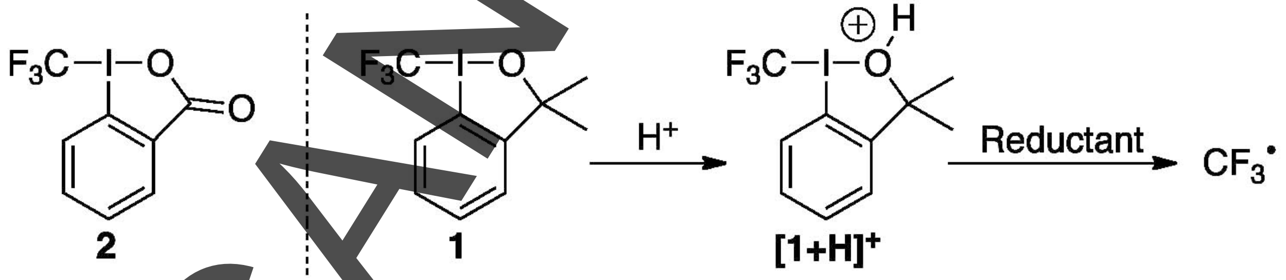
[(a)] ETH Zürich, INSTITUTE OF INORGANIC CHEMISTRY - ZÜRICH (SWITZERLAND)
[(b)] ETH ZÜRICH, LAC - ZÜRICH (SWITZERLAND)

* santschi@inorg.chem.ethz.ch

Since the advent of hypervalent iodine based electrophilic trifluoromethylating reagents (1, 2) in 2006 a plethora of nucleophiles have been successfully targeted. Only recently, however, involvement of intermediary $CF_3$ radicals was proposed in a study concerning the functionalization of allylic substrates [1].

By studying the mechanism of the electrophilic trifluoromethylation of thiophenol we identified the protonated form of reagent 1, $[1+H]^+$, as a key intermediate for the generation of $CF_3$ radicals [2]. In addition, DFT calculations at the B3LYP / aug-cc-pVTZ-pp level of theory of the frontier molecular orbitals involved further corroborated this hypothesis. Hence, after formation of $[1+H]^+$ by deprotonation of thiophenol by 1, a single electron transfer furnishes the $CF_3$ and thiyl radicals. Whereas existence of the former could be shown by TEMPO trapping experiments, the latter was amenable to EPR detection. The highly electrophilic $CF_3$ radical is then attacked by thiophenol and this new electron-excessive species may serve as reductant for 1, thus ensuring propagation.

This model mechanism not only allowed to understand results obtained in late-stage cysteine – side chain modifications in proteins but also to extend the scope of elements that may be addressed with reagent 1. This talk will present evidence for the generation of $CF_3$ radicals from 1 utilizing thiols as suitable reductants. Furthermore, the importance of protonation of 1 to give $[1+H]^+$ will be demonstrated and some applications of the mechanism presented.



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## P2.37

# Solvolysis of $SF_4$•Nitrogen Base Adducts by HF, and the Solid-State Structure of $SF_4$.

**J. GOETTEL** [(a)]*, **N. KOSTIUK** [(a)], **M. GERKEN** [(b)]

[(a)] University of Lethbridge - LETHBRIDGE (CANADA)
[(b)] UNIVERSITY OF LETHBRIDGE, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY - LETHBRIDGE (CANADA)

* jamiegoettel@gmail.com

Sulfur tetrafluoride forms Lewis acid base adducts with pyridine and its derivatives 2,6-dimethylpyridine, 4-methylpyridine and 4-dimethylaminopyridine, which have been recently identified in our lab. In the presence of HF, the nitrogen base in the $SF_4$ base reaction systems is protonated, which can formally be viewed as solvolysis products of the $SF_4\bullet$base adducts by HF. The resulting salts have been studied by Raman spectroscopy and X-ray crystallography. Crystal structures were obtained for pyridinium salts: $[HNC_5H_5^+]F^-\bullet SF_4$, $[HNC_5H_5^+][HF_2]^-\bullet 2SF_4$; 4-methylpyridinium salt: $[HNC_5H_4(CH_3)^+]F^-\bullet SF_4$; 2,6-methylpyridinium salts: $[HNC_5H_3(CH_3)_2^+]_2[SF_5^-]F^-\bullet SF_4$, $[HNC_5H_3(CH_3)_2^+]_2F^-[SF_5^-]\bullet 4SF_4$; 4-dimethylaminopyridinium salts: $[HNC_5H_4N(CH_3)_2^+]_2[SF_5^-]F^-\bullet CH_2Cl_2$, $[NC_5H_4N(CH_3)_2^+][HF_2^-]\bullet 2SF_4$; and the 4,4'-bipyridinium salts: $[HNH_4C_5{-}C_5H_4N^+]F^-\bullet 2SF_4$ (Figure 1), $[HNH_4C_5{-}C_5H_4NH^{2+}](F^-)_2\bullet 4SF_4$. These structures exhibit a surprising range of bonding modalities between $SF_4$ and $F^-$ and provide an extensive view of $SF_4$ in the solid state. The $[HNC_5H_3(CH_3)_2^+]_2F^-[SF_5^-]\bullet 4SF_4$ salt contains layers of $SF_4$. Subsequently, we were able to obtain an X-ray crystal structure of neat $SF_4$. The solid-state structure of this important binary main-group fluoride has been subject of many speculations and attempts to obtain the crystal structure had failed in the past.

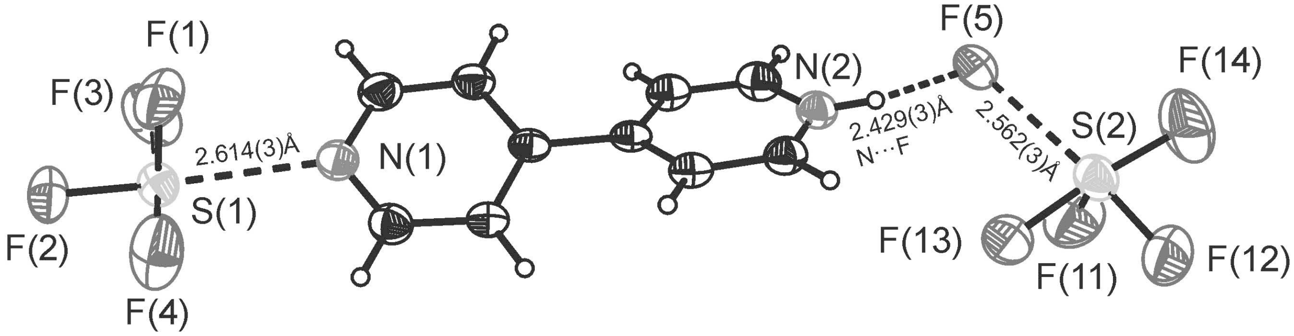


*Figure 1 Thermal ellipsoid plot of [F4S---NC5H4-C5H4NH+]F- SF4*

## P2.38

# New Fluorine-Containing Antimony(III) Complexes in the System NaNCS – $SbF_3$ – $H_2O$: Composition, Structure, and Properties

**L. ZEMNUKHOVA** [(a)], **A. UDOVENKO** [(a)], **N. MAKARENKO** [(a)*], **A. PANASENKO** [(a)], **V. KAVUN** [(b)]

[(a)] Institute of Chemistry, FEB RAS - VLADIVOSTOK (RUSSIA)
[(b)] Institute of Chemistry, FEB RAS, NMR LAB. - VLADIVOSTOK (RUSSIA)

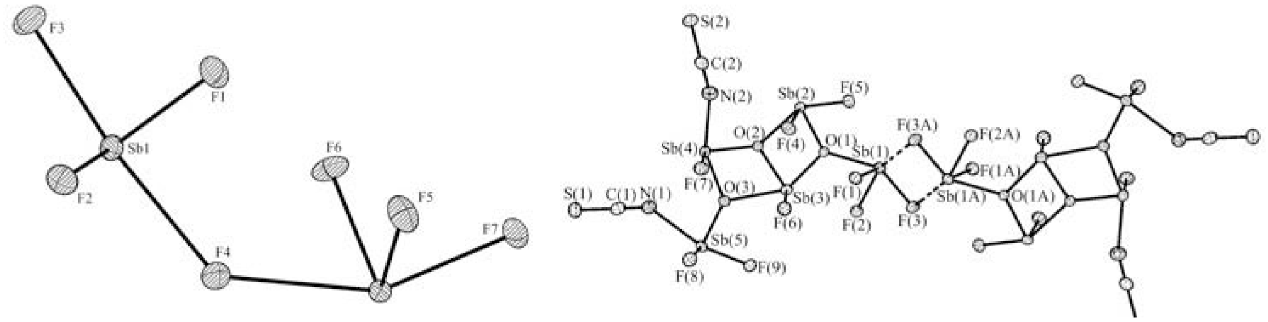
* makarenko@ich.dvo.ru

New antimony(III) fluorocomplexes of compositions $Na_2Sb_5F_9O_3(NCS)_2$ and $NaSb_2F_7{\cdot}H_2O$ were synthesized from aqueous solutions of NaNCS and $SbF_3$. The complexes structures and physical-chemical properties were studied by means of the methods of chemical, X-ray structural, and thermal analysis as well as IR, $^{121,123}$Sb NQR, and $^{19}$F NMR spectroscopy.

Interaction of antimony trifluoride with sodium thiocyanate was carried out in an aqueous solution in the components molar ratios range 0.25–1:1. At a molar ratio of 0.25:1, the fluoride complex $NaSb_3F_{10}$ of the known crystal structure [1] crystallizes from the solution. The increase of the NaNCS : $SbF_3$ ratio up to 0.5:1 results in the formation of large colorless crystals of a composition in compliance with the formula $NaSb_2F_7{\cdot}H_2O$ (I). This compound is the first crystal hydrate in the group of complex heptaantimonates(III) with single-valence cations. A fine-crystal colorless oxocyanofluoride antimony(III) compound of a composition $Na_2Sb_5F_9O_3(NCS)_2$ (II) is formed from a solution containing sodium thiocyanate and antimony trifluoride at the equimolar ratio. The compounds were obtained from solutions in the forms of single crystals, which enabled us to determine their crystal structures.

The structure of the complex compound (I) is built from $Na^+$ cations, $H_2O$ molecules, and asymmetric dimer complex anions $[Sb_2F_7]^-$ (Fig. 1). The anions are composed of two trigonal bipyramids $[SbEF_4]$ with a lone electron pair E linked through the bridge fluorine atom.

The complex $Na_2Sb_5F_9O_3(NCS)_2$ (II) has a layered crystal structure composed of $Na^+$ cations and ten-nuclei complex anions $[Sb_{10}F_{18}O_6(NCS)_4]^{4-}$ (Fig. 2), which, in their turn, are composed of two five-nuclei anions $[Sb_5F_9O_3(NCS)_2]^{2-}$ linked through weak ionic bonds Sb–F 2.529(2) Å. Ten-nuclei complex anions are linked to each other with formation of layers through Sb···F secondary bonds and Na–F bonds. These layers are combined into a framework by van der Waals forces.



*Left: Dimer complex anion in the structure of I. Right: Symmetric complex anion in the structure of II*

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P2.39

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# The Study of Interaction Between $UF_6$ and Dimethyl Ether

**E. ATAKHANOVA [a], V. OREKHOV [a], A. RYBAKOV [a], V. SHIRYAEVA [a]***

[a] JSC «Leading Scientific Research Institute of Chemical Technology» - MOSCOW (RUSSIAN FEDERATION)

* shiryaeva_vv@mail.ru

We make systematic research of interaction between $UF_6$ and various classes of organic substances [1], in particular with saturated and unsaturated hydrocarbons in gaseous phase. It is well known saturated hydrocarbons react with $UF_6$ reducing it up to $UF_4$ and themselves become partially resinified. Chlorine atoms introduction in organic molecule prevents the process of resinifying and makes it possible to get $UF_4$ of high qualityand fluorinechlorinesubstituted hydrocarbons[1]:

$CH_3{-}CF_3 + UF_6 \rightarrow CH_2F{-}CF_3 + HF + UF_4$.

During the interaction of $UF_6$ with unsaturated hydrocarbons and their halogenated derivatives the reaction occurs according to the following mechanism:

$>C=C< + UF_6 \rightarrow >CF{-}FC< + UF_4$.

From our point of view it is of interest to study the interaction between $UF_6$ and the primary specimen of ethers – dimethyl ether $(CH_3)_2O$. On the one hand this compound can be regarded as the analogue of water molecule and on the other – as the analogue of halogen containing aliphatic compounds as a result of similar properties of halogen and oxygen atoms.

As is well known $UF_6$ interaction with water follows the reaction:

$UF_6 + 4H_2O \rightarrow UO_2F_2 + 4HF$,

and with halogen containing aliphatic compounds:

$2UF_6 + CH_2Cl_2 \rightarrow 2UF_4 + CF_2Cl_2 + 2HF$.

It was determined that when the temperature is below 350°C the reaction with $Me_2O$ proceeds to the formation of $UF_4$, and when the temperature increases to 550°C – to the production of $UO_2$ [2]. Then we discuss the mechanisms of reaction proceeding in examined temperature interval from 300 to 600°C.

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[2] Patent of Russian Federation №2414428 \"Method of synthesis uranium oxides from uranium tetrafluoride\" with priority from august 5, 2009.

## P2.40

# Dynamic Orientational Disorder in Seven-coordinated Fluoro- and Oxofluorometallates

**N. LAPTASH** [(a)]*, **A. UDOVENKO** [(a)]

[(a)] Institute of Chemistry Far Eastern Branch of RAS - VLADIVOSTOK (RUSSIA)

* laptash@ich.dvo.ru

Seven-coordinated species which could exist either as a monocapped octahedron (CO), a monocapped trigonal prism (CTP), or a pentagonal bipyramid (PB) are of particular interest and considered to be stereochemically nonrigid, since interconversion between the three geometrical arrangements of ligaqnds can occur without difficulty. Tetragonal crystal structures of $Rb_2TaF_7$ and $(NH_4)_2TaF_7$ were determined. CTP and BP configurations of $TaF_7^{2-}$ coexist at room temperature as a result of strong intraspheric dynamics of Berry pseudorotation type. These polyhedra are highly distorted (Figure 1). Upon cooling, $Rb_2TaF_7$ undergoes the phase transition (145 K) of the first order, and seven-coordinated polyhedron transforms into regular CTP. The seven-coordinated polyhedron in $(NH_4)_2TaF_7$ approaches the BP configuration as the temperature decreases.

Crystal structures of seven-co ordinated elpasolite-like $(NH_4)_3ZrF_7$ and $(NH_4)_3NbOF_6$ were refined with respect to the problem of abnormally short F–F distances in pentagonal bipyramid which was solved by choosing a non-centrosymmetric space group of F23 instead of Fm3m.

Cubic elpasolite-like $Rb_3TaOF_6$ is characterized by the existence of non-rigid $TaOF_6^{3-}$ polyhedron with synchronous Ta–O Ta–F vibrations appearing as the infrared band at 720–730 $cm^{-1}$.

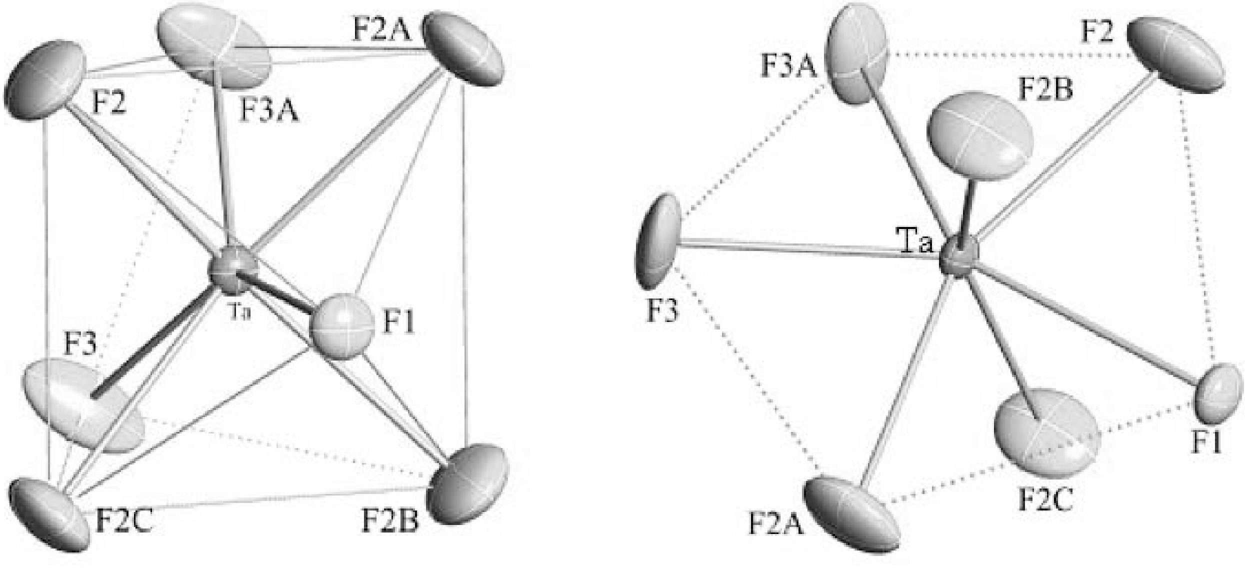


*Figure 1. Seven-coordinated polyhedron in $(NH_4)_2TaF_7$ as intermediate configuration between CTP (left) and PB (right).*

## P2.41

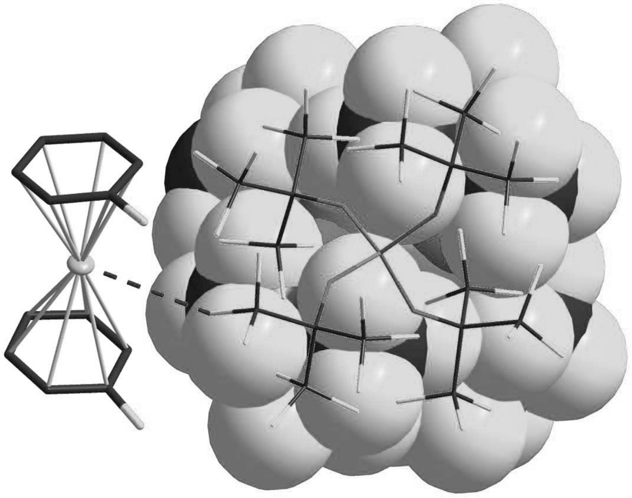
# Applied Gallium(I) Chemistry – Synthesis of Highly Reactive Polyisobutylene

**M.R. LICHTENTHALER** [(a)*], **I. KROSSING** [(a)]

[(a)] University of Freiburg, Institute for Inorganic and Analytical Chemsitry - FREIBURG IM BREISGAU (GERMANY)

* martin.lichtenthaler@ac.uni-freiburg.de

Low molecular weight polyisobutylene (PIB) is one of the most important isobutylene (IB) polymers. Its main application – an essential intermediate for manufacturing additives for lubricants and fuels – relies on the PIB being highly reactive (HR-PIB). This means that the polymer features a content of terminal olefinic double bonds higher than 60 mol%. Though many syntheses of HR-PIB have been reported in the past, most of them feature a lack: e.g. low reaction temperatures, dichloromethane as solvent, long reaction times or high concentrations of the initiating/catalyzing species.



*Molecular structure of $[Ga(C_6H_5F)_2]^+[Al(OC(CF_3)_3)_4]^-$ (excerpt of the crystal structure).*

In 2010 a simple route to univalent gallium salts of weakly coordinating anions (WCAs) was developed by Slattery et al. Herein, the gallium(I) cations are $\eta^6$-coordinated by two ligands in a bent sandwich fashion and weakly interact with the WCAs.

Recently, a number of reactions showed the superior quality of the univalent gallium salts initiating or catalyzing the polymerization of IB. Thus, the synthesis of HR-PIB can be carried out at relatively high reaction temperatures up to +10 °C, in the non carcinogenic solvent toluene as well as using relatively low concentrations of the initiating/catalyzing species down to 0.007 mol%. Furthermore, the reactivity can be tuned by replacing the aromatic ligands with electron-rich/poor analogs. The experimental results were backed by quantum-chemical calculations giving a first hint on a cationic polymerization mechanism.

## P2.42

# Synthesis and characterization of alkali metal compounds containing $([TiF_5]^-)_n$, $([Ti_2F_9]^-)_n$, and the new discrete $[Ti_8F_{36}]^{4-}$ anion

**I.M. SHLYAPNIKOV** [(a)], **E.A. GORESHNIK** [(a)], **Z. MAZEJ** [(a)]*

[(a)] Jožef Stefan Institute, DEPARTMENT OF INORGANIC CHEMISTRY AND TECHNOLOGY - LJUBLJANA (SLOVENIA)

* zoran.mazej@ijs.si

Crystallizations between alkali metal fluorides and $TiF_4$ in anhydrous HF in a different molar ratios yielded the single crystals of $Rb_2TiF_6$, $CsTiF_5$, $ATiF_5$•HF (A = Na, K, Rb), $NaTi_2F_9$•HF, $K_4[Ti_8F_{36}]$•6HF and $Rb_4[Ti_8F_{36}]$•8HF. Additionally, $ATiF_5$ (A = Na, K) and $NaTi_2F_9$ were synthesized and characterized.

The main structural feature of $ATiF_5$ and $ATiF_5$•HF compounds is formed by infinite zig-zag $([TiF_5]^-)_n$ chains of distorted $[TiF_6]$ octahedra joined *via cis* vertices. Raman spectrum of $CsTiF_5$ entirely matches in the literature reported Raman spectrum of $Cs_2[Ti_2F_{10}]$ [1] for which it was suggested that it consists of discrete $([Ti_2F_{10}]^{2-})$ anions and $Cs^+$ cations. On the basis of obtained results it can be concluded that previously reported $Cs_2[Ti_2F_{10}]$ is in fact $CsTiF_5$ consisting from infinite zig-zag $([TiF_5]^-)_n$ chains and $Cs^+$ cations.

The $([Ti_2F_9]^-)_n$ salts contain polymeric $([Ti_2F_9]^-)_\infty$ anions, as already observed in $CsTi_2F_9$ [2], which appear as two parallel infinite zig-zag chains comprised of $TiF_6$ units where each $TiF_6$ unit of one chain is connected to a $TiF_6$ unit of the second chain through a shared fluorine vertex.

Crystallizations of AF (A = K, Rb) and $TiF_4$ (starting molar ratio AF : $TiF_4$ = 1 : 2) from aHF solutions yield single crystals of $K_4Ti_8F_{36}\cdot 8HF$ and $Rb_4Ti_8F_{36}\cdot 6HF$. Their crystal structure determinations showed that both structures contain previously unknown octameric $[Ti_8F_{36}]^{4-}$ anions constructed from eight $TiF_6$ octahedral units connected into a cube.

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## P2.43

# Application of Bromine Trifluoride or Potassium Tetrafluorobromate for Determination of Trace Elements in High Purity Optical Materials

**V.N. MITKIN** [(a)]*, **D.Y. TROITSKII** [(a)], **A.K. SAGIDULLIN** [(a)], **A.I. SAPRYKIN** [(a)]

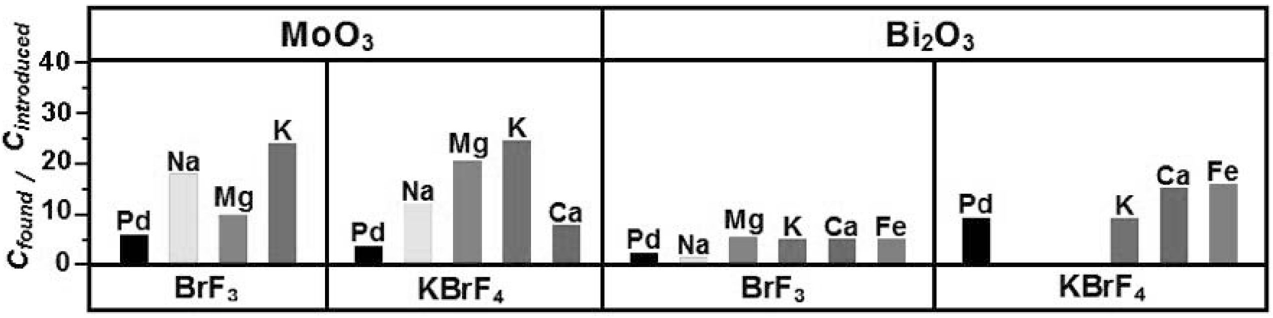
[(a)] NIKOLAEV INSTITUTE OF INORGANIC CHEMISTRY OF SB RAS - NOVOSIBIRSK (RUSSIA)

* mit48@mail.ru

The need of high purity optical materials such as bismuth (III) oxide and molybdenum (VI) oxide is an important requirement. So the determination of trace elements in these materials becomes a real priority. The aim of the present work is the use of $BrF_3$ or $KBrF_4$ for fluorination of oxide substrate followed by sublimation of the formed fluorinated species . The temperature of sublimation was investigated too. $BrF_3$ could be used below 80-120°C whereas $KBrF_4$ was used as a source of $BrF_3$ vapor around 360-380°C. The amount of impurities was testedinto the $MoO_3$ or $Bi_2O_3$ oxides with optical grade together with a reference specimen of palladium. Samples were used as tablets and placed on teflon disk to be reacted ith $BrF_3$, or on nickel foil for the thermolysiswith $KBrF_4$. The packed sample was placed into glassy-carbon cruciblesfor fluorination. The fluorinationof 0.6 g $MoO_3$ and 0.9 g $Bi_2O_3$ was carried out for 2-3 hours at 80-120°C and 360-380°C, respectively. Simultaneously the sublimation of the fluorinated oxide substrate occurred. It was found that the weight of the tablets of $MoO_3$ and $Bi_2O_3$ have been reduced to 0.3 and 0.5 g, respectively.

The change of content of added elements in the investigated samples under the fluorination and sublimation was controlled by laser ionization mass-spectrometry method (LMS) using mass-analyzer EMAL-2.The limits of detection of about 20 trace elements was at $10^{-6}$ – $10^{-4}$ wt.%level. The presence of Na, Mg, K, Ca, Fe impurities concentration after fluorination was confirmed with the increase of palladium content of 6 and 4 times following the fluorination of $MoO_3$ sample with $BrF_3$ or $KBrF_4$, respectively. Whereas under the fluorination of $Bi_2O_3$ samples, the change of palladium content was in 0,5 and 9 times after the fluorination with $BrF_3$ or $KBrF_3$, respectively. The corresponding change of Na, Mg, K, Ca, Fe content in the different samples estimated in the network of LMS confidence interval are shown in a Fig. 1.

The new scheme of $MoO_3$ and $Bi_2O_3$ pre-sampling for concentration of trace elements stated in this work is quite universal because the fluorides of many trace elements do not sublimate at rather low temperature and small fluorination durations. The method presented is a good alternative to the traditional "wet chemical" methods.



*Concentration of microelements in $MoO_3$ and $Bi_2O_3$ samples after fluorination*

## P2.44

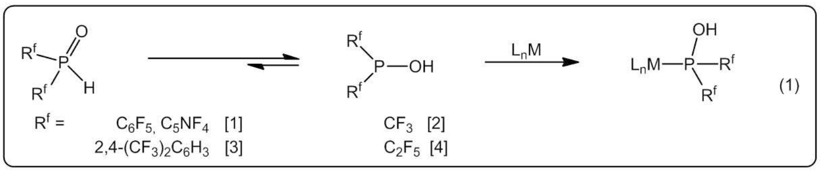
# Transition Metal Complexes of Phosphinous and Phosphonous Acids

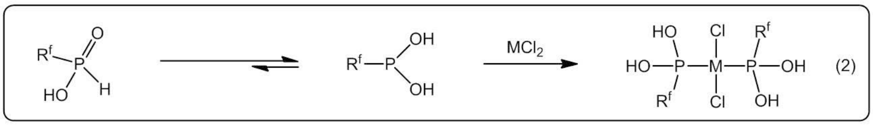
**N. ALLEFELD** [(a)*], **B. KURSCHEID** [(b)], **N.V. IGNAT'EV** [(c)], **B. HOGE** [(a)]

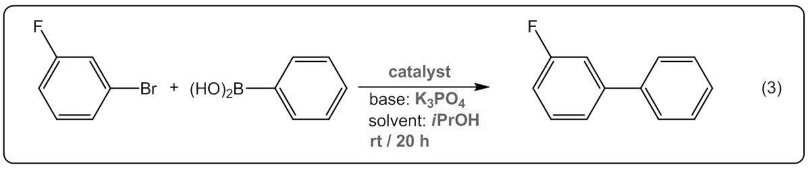
[(a)] Bielefeld University, Anorganic Chemistry II - BIELEFELD (GERMANY)
[(b)] Bielefeld University - BIELEFELD (GERMANY)
[(c)] Merck KGaA, PM-ABE - DARMSTADT (GERMANY)

* nadine.allefeld@uni-bielefeld.de

Diorganylphosphinous acids, $R_2POH$, are in principle not stable with respect to their tautomeric counterparts $R_2P(O)H$. The stabilization of phosphinous acids can be achieved either with electron withdrawing substituents [1-4] or by the coordination to transition metals.[5] Phosphinous acid complexes exhibit a high catalytic activity in Suzuki-type reactions.[6]







For a technical application as a catalyst in a two-phase system with water, water soluble complexes are desirable. This can be achieved by substitution of one $R^f$-group with an OH function. Phosphinous acids, $(R^f)_2POH$, are quite sensitive to hydrolysis, leading to the formation of the phosphinic acid derivative, $R^fPH(O)(OH)$, which is in a tautomeric equilibrium with the phosphonous acid $R^fP(OH)_2$.

In general the equilibrium is on the side of the phosphinic acid, but the phosphonous acid can be trapped by coordination to transition metals. The reaction with $PdCl_2$ and $PtCl_2$ leads to the formation of water soluble phosphonous acid complexes which show a promising activity in Suzuki-type reactions.

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## P2.45

# Titanium-Catalyzed C-F Bond Activation of Fluoroalkenes and Fluoroarenes

**J. KRÜGER** [(a)]*, **M.F. KÜHNEL** [(b)], **D. LENTZ** [(c)]

[(a)] FREIE UNIVERSITÄT BERLIN, ANORGANISCHE CHEMIE - BERLIN (GERMANY)
[(b)] FREIE UNIVERSITÄT BERLIN - BERLIN (GERMANY)
[(c)] FREIE UNIVERSITÄT BERLIN, Institut für Chemie und Biochemie - BERLIN (GERMANY)

* juliane.krueger@fu-berlin.de

The unique properties of organofluorine compounds like hydrophobicity and metabolic stability have led to remarkable progresses in medicinal chemistry. [1] However it remains still a challenge to create suitable synthons. There is of course the potential to introduce fluorine via a direct approach, but sometimes this is not possible. In such cases it would be better to selectively hydrodefluorinate the perfluorinated compound to get the desired product. Recently we reported the first titanium-catalyzed C-F activation of fluoroalkenes. [2] Based on these results we applied the catalytic system to other substrates containing different types of fluorine atoms. In total we studied the hydrodefluorination (HDF) of functionalized fluoroarenes and -alkenes with respect to scope and selectivity of the reaction (fig. 1). [3]

In all reactions we used similar HDF conditions with 1-5 mol% catalyst loading and 1.1 equivalents diphenylsilane as a hydride source. We obtained the corresponding HDF products in very good yields. The selectivity and turnover numbers are depending on the substrates. Mechanistic studies indicate a titanium(III) hydride as the active species, which forms a titanium(III) fluoride by H/F exchange with the substrate. The HDF step can progress over an insertion/elimination or a s-bond metathesis mechanism.

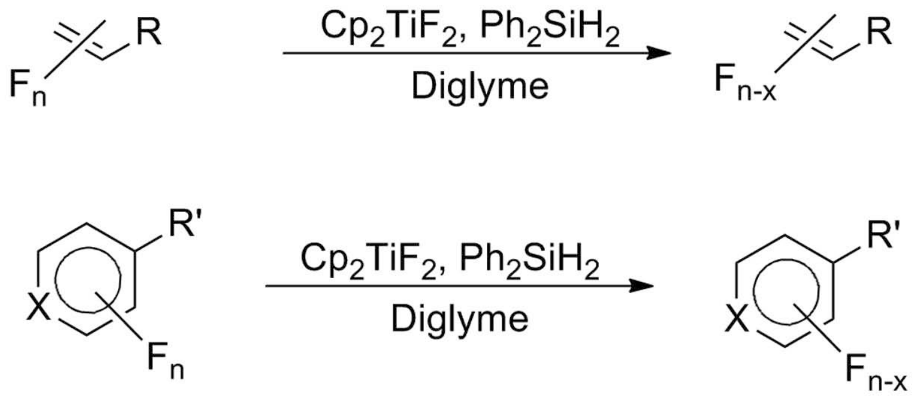

*Fig. 1. Catalytic HDF of fluoroalkenes and -arenes, with R = H, F, CF3, C6H5, ferrocenyl-; X = CF2, N and R' = F, CF3, Br, morpholino-, C6F5.*

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## P2.46

# Mercury ion as a center for coordination of $XeF_2$ ligand

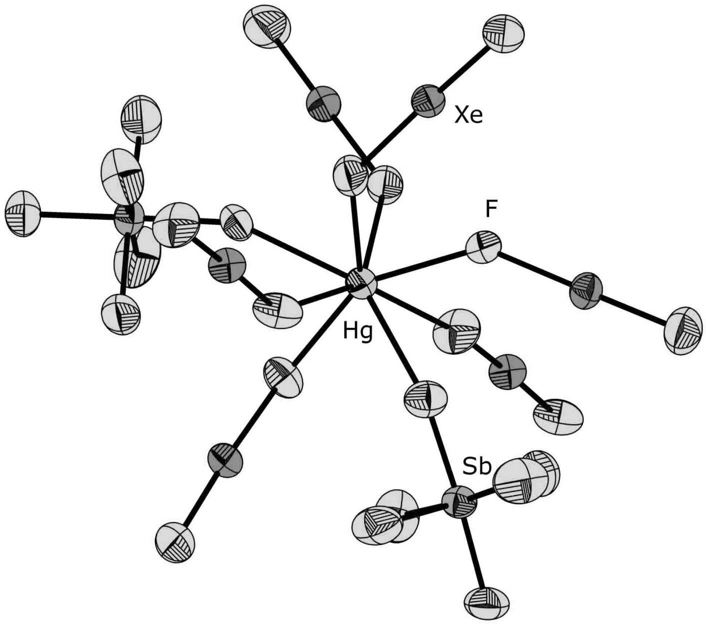
**G. TAVCAR** [(a)]*, **E.A. GORESHNIK** [(b)]

[(a)] Jožef Stefan Institute - LJUBLJANA (SLOVENIA)
[(b)] Jožef Stefan Institute, DEPARTMENT OF INORGANIC CHEMISTRY AND TECHNOLOGY - LJUBLJANA (SLOVENIA)

* gasper.tavcar@ijs.si

Xenon difluoride, as a ligand bonded directly to a metal ion, was first prepared by Hagiwara in 1991,[1]and a variety of further metal salts with $XeF_2$ coordinated to metal ions have been discussed in recent review.[2] Form the group 12 only $XeF_2$ coordination compounds with zinc [3] or cadmium [4] as metal ions are published.

Our work was focused on mercury compounds with different fluoro anions, in which $XeF_2$ can coordinate to the metal ion. We were able to prepare a variety of complexes with $XeF_2$ ligand, where the amount of coordinated $XeF_2$ can be influenced by the concentration of the ligand in the reaction solution. All the compounds were characterized by Raman spectroscopy and some crystal structures were determined.



*The coordination sphere of mercury in $[Hg(XeF_2)_5](SbF_6)_2$.*

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## P2.47

# In situ cryocrystallization of halogen bonded supramolecular adducts

**G. TERRANEO** [a]*, **P. METRANGOLO** [a], **G. RESNATI** [a], **G. CAVALLO** [a], **J. LIN** [a]

[a] NFMLAB-DCMIC “Giulio Natta”, Politecnico di Milano, NFMLAB - DEPT OF CHEMISTRY, MATERIALS AND CHEMICAL ENGINEERING - MILANO (ITALY)

* giancarlo.terraneo@polimi.it

*In situ* crystallization of liquids and gases has been applied to the growth and study of the crystal structures of a number of molecular liquids and gases and their mixtures. This technique has demonstrated to be fundamental to study weak and elusive interactions (e.g. weak hydrogen bonds, halogen•••halogen contacts, etc.) in supramolecular structures, polymorphs and functional materials [1].

Halogen bond (XB) has consolidated its status an effective and reliable tool in crystal engineering involving perfluorinated systems [2].

Strong XBs have been the object of extensive crystallographic studies and detailed information are available on the structural profile of these interactions. Weaker XBs have received much less attention, as they give rise to less reliable supramolecular synthons and it is more likely that weak and ubiquitous interactions frustrate the crystal packing design. Numerous structures in the Cambridge Structural Database prove that C-X•••O interactions (X = Br or Cl), typical weak XBs, are able to influence the crystalline packing. However details on structural features and role of the C-X•••O supramolecular synthon can be hardly surmised from these structures as nearly all of them were obtained serendipitously and/or involve quite complex and random molecules.

In this communication we report a structural study using *in situ* cryocrystallization technique of dihaloperflurorocarbons and their halogen bonded adducts formed with systems having an oxygen atom as halogen bonding acceptor [3]. These tectons have been chosen to maximize the possibility that the crystal structure gives reliable indications on the X•••O synthon and its role in driving the self-assembly process.

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## P2.48

# Fluorocarbon moieties affect crystals structures

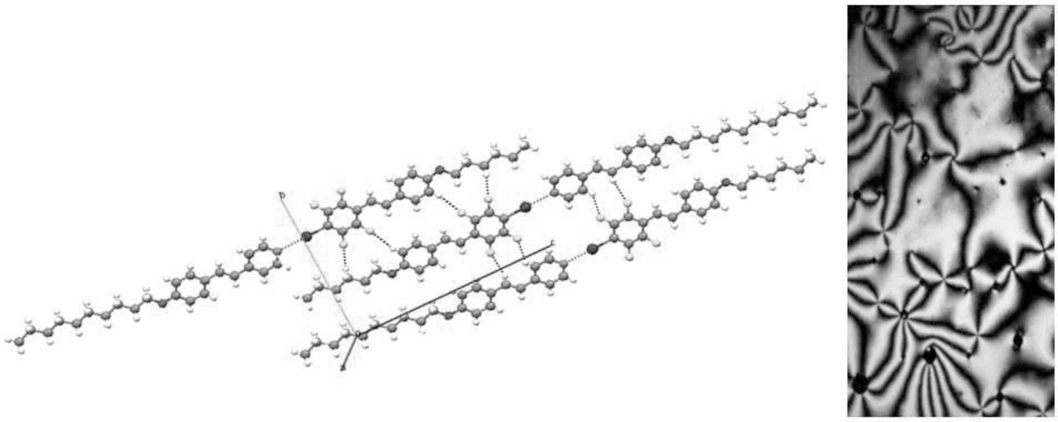
**G. RESNATI** (a)*, **G. CAVALLO** (a), **P. METRANGOLO** (a)*, **G. TERRANEO** (a), **L. COLOMBO** (a)

(a) NFMLAB-DCMIC "Giulio Natta", Politecnico di Milano, NFMLAB - DEPT OF CHEMISTRY, MATERIALS AND CHEMICAL ENGINEERING - MILANO (ITALY)

* pierangelo.metrangolo@polimi.it

Perfluorocarbon moieties are endowed with unique aggregation features. Relative to other heteroatoms, the fluorine atom has a weak tendency to give attractive interactions and this atomic property is possibly related to the "omniphobic" character of perfluoroalkane derivatives [1]. Perfluoroaryl residues have a quadrupolar moment opposite to that of their hydrocarbon parents and this accounts for the strong π•••π staking interactions perfluoroarenes often give rise to.

In this communication it will be described how a cooperative interplay of the unique aggregation features of perfluorocarbon derivatives and the strong halogen bond given by the heavier halogen atoms in iodo- and bromoperfluorocarbons [2] allows for the hierarchical organization of molecular components into heteromeric solid architectures. The relationship between the "omniphobic" character of perfluoroalkanes and crystals packing will be discussed. The segregation typical for hybrid perfluoroalkane/alkane systems controls the packing of 0D, 1D, and 2D adducts formed by strong attractive interactions, e.g. halogen bond, into the layered architectures of hybrid solid systems in the bulk. Some superfluorinated ionic liquid crystals showing such layered structures will be described. We will discuss the correlation between the crystal structure of the supramolecular materials thus obtained and their functional properties. It will shown how the halogen bond drives the formation of dimers and trimers when alkoxystilbazoles interact with mono- and diiodoperfluoroalkanes and -arenes. These oligomers further organize into 2D and 3D architectures under control of the segregation of perfluoroalkyl chains or the C-H•••F-C hydrogen bond involving aromatic and perfluoroaromatic residues (Figure, left). While the single pure molecular components do not show any mesomorphic property, the obtained heteromeric architectures described above do show liquid crystalline properties (Figure, right) which disappear on architecture disruption.



*X-ray structure of n-decyloxystilbazole/n-hexyloxystilbene dimer (left) and optical microscope image of its nematic phase (right).*

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## P2.49

# New method of metal fluorides synthesis with using beta-cyclodextrin

**A. FEDOROVA** [(a)]*, **S. ARKHIPENKO** [(b)], **A. FEDULIN** [(b)], **I. MOROZOV** [(b)]

[(a)] LOMONOSOV MOSCOW STATE UNIVERSITY, CHEMISTRY DEPARTMENT - MOSCOW (RUSSIA)
[(b)] LOMONOSOV MOSCOW STATE UNIVERSITY - MOSCOW (RUSSIA)

* annaaf@mail.ru

Alkaline earth and rare earth element fluorides attract attention of researchers because of wide possibilities of their applications: they can be used as carriers for catalysts and as efficient luminescent materials. So, $NaYF_4$, doped by $Yb^{3+}$ and $Er^{3+}$, is one of the most effective up-converters.

We propose a new method for simple and complex metal fluorides synthesis by decomposing metal trifluoroacetate hydrates in the presence of beta-cyclodextrin (b-CD). Capabilities of the method are demonstrated in a number of examples: 1) the synthesis of simple fluorides with large surface area ($MgF_2$, $CaF_2$), 2) the preparation of solid solutions $RF_3$-$CaF_2$ (R = Yb, Nd), 3) the synthesis of single-phases $M_2RF_7$, $M_4R_3F_{17}$ (M – Ca, Ba) and 4) the preparation of complex fluoride $NaYF_4$, doped by $Yb^{3+}$ and $Er^{3+}$.

1) It was shown that the decomposition of metal trifluoroacetates in the presence of b-CD allows to produce $MgF_2$ and $CaF_2$ with a large surface area (~60-80 $m^2g^{-1}$) despite relatively long heating at 400 °C.

2) In addition, this method allows to obtain the solid solutions of fluorides which was shown by the example of $Ca_{1-x}R_xF_{2+x}$ (R = Yb, Nd). The formation of solid solutions with a homogeneous distribution of the elements was confirmed by XRD, X-ray microanalysis and X-ray fluorescence analysis.

3) This method of synthesis has also been successfully applied to obtain multiple metal fluorite-type phases $M_2RF_7$, $M_4R_3F_{17}$, (M = Ca, Sr, Ba; R =Yb, Nd) and 4) complex fluorides $NaYF_4$, doped by $Yb^{3+}$ and $Er^{3+}$.

It should be noted that decomposition of the corresponding metal trifluoroacetates without b-CD in the examples 2) and 3) does not lead to the formation of solid solutions and complex fluorides, and the formation of a mixture of simple metal fluorides was observed. In the case of $NaYF_4$ samples obtained in the presence of b-CD are more homogeneous in composition and have more uniform pore size distribution than those obtained without b-CD. At the same time, the addition of b-CD prevents the pyrohydrolysis process.

In conclusion, we have developed a new soft chemistry synthetic method for preparation of simple and complex metal fluorides and solid solutions of fluorides with a homogeneous distribution of the elements. Advantages of this method are simplicity, availability of precursors and low temperature of the process.

## P2.50

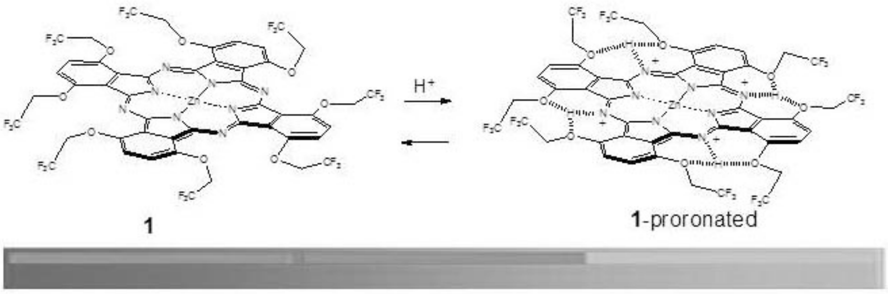
# Trifluoroethoxy Semi-coated Phthalocyanine Indicates Super Sensitive Solvatochromic Behaviour in Solvents

**E. TOKUNAGA** [a]*, **S. MORI** [b], **N. SHIBATA** [a]

[a] NAGOYA INSTITUTE OF TECHNOLOGY, DEPARTMENT OF FRONTIER MATERIALS - NAGOYA (JAPAN)
[b] NAGOYA INSTITUTE OF TECHNOLOGY - NAGOYA (JAPAN)

* tokunaga.etsuko@nitech.ac.jp

Phthalocyanines are popular as artificial dyes and pigments in the textile, printing, and paint industries due to their high thermal stability and low reactivity, since the discovery in the 1930s by Linstead and Robertson. In recent years, phthalocyanines have attracted much attention as functional dyes due to their unique electronic and optical properties in many high technology fields, including dye-sensitized solar cells, photochromic dyes, anticancer agents for photodynamic therapy, electrochromic devices, information storage systems, and more. The optical properties of phthalocyanines highly depend on the nature of outer peripheral substitution of phthalocyanines. Incidentally, our group has focused on the development of novel fluorinated compounds for material science and pharmaceutical chemistry in future a market. Over past five years, we have reported the design and synthesis of a series of trifluoroethoxy (TFEO) phtalocyanines. All the fully-coated TFEO-phtalocyanines developed show very unique behaviour of absolute non-aggregation. During our research program in this field, we came across the super solvatochromic behaviour of zinc 1,4,8,11,15,18,22,25-octakis(2,2,2-trifluoroethoxy)phthalocyaninate (1). The chromism of 1 is based on a change in the solvent character and its concentration, which can be detected by the naked eye (Fig. 1). The property of 1 was investigated using UV-Vis, transmission and steady-state fluorescence spectra. In line with our expectation on the basis of previous experience on TFEO-full-coated Pcs, 1 exhibits strong absorption at 710 nm of the Q-band, and 352 nm of the B-band with a small peak at 768 nm in CHCl3 solution (1.0 x 10-4 M) , which are attributed to the non-aggregated monomer. UV-Vis spectra of 1 taken as a solid thin film also indicated its non-aggregation status. MALDI-TOF MS spectrometry of 1 in solid state showed that the expected molecular ion (m/z 1361), represents a monomer molecular ion peak. These results clearly supported that semi TFEO-coating mainly exists as an aggregation-free monomer, even in the solid state. To our great surprise, this aggregation-free Pc 1 was spontaneously transformed to form a protonated structure upon dilution (1.0 x 10-5 to 10-7 M), resulting in a shift in red at 768 nm and 725 nm absorption. The protonation was confirmed by changes observed in spectra recorded with the addition of pyridine to afford a complete aggregation-free monomer. The concentration dependent protonation properties are completely different from those of fully- coated Pcs. The unexpected effects of TFEO semi-coating on Pc led us to evaluate whether the fluorine was actually playing a main role of the character. The details will be discussed in the presentation.



## P2.51

# The Reactions of the $Xe_3OF_3^+$ Cation with $ClO_2F$ and $BrO_2F$; the Syntheses and Structural Characterization of $FXeOClO_3$ and $[ClO_2][AsF_6].2XeF_2$

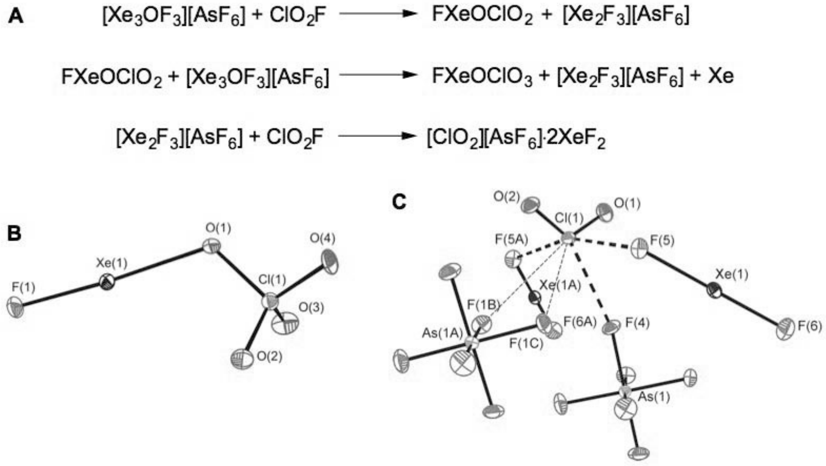
**J. HANER** [(a)*], **M. ELLWANGER** [(a)], **H.P.A. MERCIER** [(a)], **G.J. SCHROBILGEN** [(a)]

[(a)] DEPARTMENT OF CHEMISTRY, McMaster University - HAMILTON (CANADA)

* hanerj@mcmaster.ca

The $FXeOXeFXeF^+$ ($Xe_3OF_3^+$) cation [1] has now been shown to function as both an "$FXeO^-$" synthetic equivalent and a powerful oxygen atom transfer reagent. The reaction of $Xe_3OF_3^+$ with liquid $ClO_2F$ yielded the corresponding xenon(II) fluoride perchlorate, $FXeOClO_3$,and the $XeF_2$ coordination complex of $ClO_2^+$, $[ClO_2][AsF_6]{\cdot}2XeF_2$ (Figure 1A). The proposed reaction pathway involves the oxidation of the transient chlorate, $FXeOClO_2$, to $FXeOClO_3$ by $Xe_3OF_3^+$. The corresponding reaction of $BrO_2F$ with $Xe_3OF_3^+$ is under investigation and will also be discussed.

The perchlorate, $FXeOClO_3$, has been fully characterized for the first time by low-temperature $^{19}F$ and $^{129}Xe$ NMR spectroscopy (−60 °C) in liquid $ClO_2F$ and in the solid state by low-temperature Raman spectroscopy (−150 °C) and single-crystal X-ray diffraction (−173 °C; Figure 1B). The other major reaction product, $[ClO_2][AsF_6]{\cdot}2XeF_2$, was crystallized from $ClO_2F$ and HF and characterized by low-temperature Raman spectroscopy and single-crystal X-ray diffraction (Figure 1C).



*(A) Formation of $FXeOClO_3$ and $[ClO_2][AsF_6]{\cdot}2XeF_2$. (B) Crystal structure of $FXeOClO_3$. (C) Crystal structure of $[ClO_2][AsF_6]{\cdot}2XeF_2$*

Each $ClO_2^+$ center coordinates two $XeF_2$ molecules through bridging Cl---F contacts that are significantly shorter than the sum of the Cl and F van der Waals radii.

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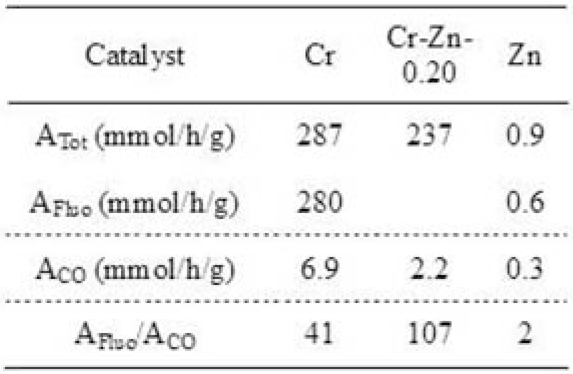
## P2.52

# Gas phase fluorination of trichloroacetyl chloride in the presence of various heterogeneous catalytic systems

**T. CORRE** [(a)], **F. METZ** [(b)], **S. BRUNET** [(a)]*

[(a)] IC2MP, UMR 7285 - POITIERS (FRANCE)
[(b)] Solvay Recheches CRTL - ST FONS (FRANCE)

* sylvette.brunet@univ-poitiers.fr



| Catalyst | Cr | Cr-Zn-0.20 | Zn |
|---|---|---|---|
| $A_{Tot}$ (mmol/h/g) | 287 | 237 | 0.9 |
| $A_{Fluo}$ (mmol/h/g) | 280 | | 0.6 |
| $A_{CO}$ (mmol/h/g) | 6.9 | 2.2 | 0.3 |
| $A_{Fluo}/A_{CO}$ | 41 | 107 | 2 |

*Table 1: Transformation of trichloroacetyl chloride over chromium based catalysts (T = 300°C, Patm)*

A significant amount of compounds with biological activity (therapeutic and / or plant) contain one or more atom (s) of fluorine, mainly as atomic or -$CF_3$ group. Trifluoroacetic acid is widely used in organic synthesis as building blocks for trifluoromethylation reactions. Trifluoroacetic acid is prepared by catalytic fluorination of trichloroacetyl chloride in the presence of a chromium oxide based catalyst and hydrogen fluoride (HF) as a fluorinating agent to lead to the formation of trifluoroacetyl fluoride (FTFA). This compound leads to trifluoroacetic acid after a hydrolysis step. Trifluoroacetyl fluoride is obtained by successive Cl/F exchanges from the corresponding chlorinated compound. However, a decarbonylation reaction leading to the formation of CO is also involved. The aim of this work is to prepare selectively the trifluorinated compound and to minimize the decarbonylation reaction. A screening of catalysts such as chromium oxide modified with zinc has been investigated in order to prepare selectively various fluorinated intermediates. As reported previously it could be possible to modify the Lewis acidity of the active sites by the presence of zinc in small amount [1]. The acido-basic properties of the catalysts are crucial in their performances in products distribution and catalytic activity. For the transformation of trichloroacetyl chloride, the best results were obtained when 20% of zinc was introduced to chromium oxide. The total ($A_{Tot.}$) and the fluorination ($A_{Fluo.}$) activities were around the same, however the activity ($A_{CO}$) for the formation of CO was decreased. Consequently the selectivity ($A_{Fluo}/A_{CO}$) measured by the ratio between fluorination and decarbonylation activities is significantly increased (Table 1). In fact, the presence of zinc decreases the Lewis acidity of the active sites and increases their number. The fluorination reaction is then favoured over the decarbonylation reaction. All these results indicate that both reactions involve the same active sites whose strength tune both the activity and the selectivity towards trifluorinated compound.

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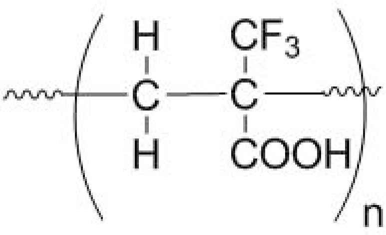
### P2.53

# Mineralization of 2-Trifluoromethacrylic Acid Polymers by Use of Pressurized Hot Water

**H. TANAKA** [(a)*], **H. HORI** [(a)], **T. SAKAMOTO** [(a)], **Y.R. PATIL** [(b)], **B. AMEDURI** [(b)]

[(a)] KANAGAWA UNIVERSITY, FACULTY OF SCIENCE - HIRATSUKA (JAPAN)
[(b)] INSTITUT CHARLES GERHARDT, IAM-ENSCM - MONTPELLIER (FRANCE)

* atsutaka32@gmail.com



Poly(MAF)-H

Since 2000, fluorochemical surfactants such as perfluoroalkyl sulfonates ($C_nF_{2n+1}SO_3^-$) have received much attention because some of them, particularly, perfluorooctanesulfonate ($C_8F_{17}SO_3^-$, PFOS) and its derivatives are ubiquitous environmental contaminants. After it became clear that they bioaccumulate in the environment, there have been efforts to develop greener alternatives. For the wider use of new fluorochemical surfactants, waste treatment techniques will have to be established for them. These chemicals may be decomposed by incineration. However, incineration requires high temperatures and it produces HF gas, which damages firebricks of the incinerators. If they could be decomposed to $F^-$ ions by means of environmentally benign techniques, the well-established protocol for the treatment of $F^-$ ions could be used: $Ca^{2+}$ is added to the system to form $CaF_2$, which is a raw material for hydrofluoric acid. Thus, the development of such techniques would allow not only for the reduction of the environmental impact, but also for the recycling of a fluorine resource, the global demand for which is increasing.

Decomposition in pressurized hot water (PHW) is an innovative and environmentally benign waste treatment technique. We previously reported that perfluoroalkylsulfonates such as PFOS are not decomposed in pure PHW, whereas they can be decomposed when iron powder is present as a reducing agent in the medium [1], and the methodology was successfully applied to the decomposition of a perfluorosulfonic acid membrane polymer for fuel cells [2] and a cyclic perfluoroalkyl surfactant [3].

Herein we report on the decomposition of 2-trifluoromethacrylic acid (MAF) polymers, that is, poly(MAF)-H and its potassium salt, poly(MAF)-K, in PHW. An effective methodology for the mineralization of these polymers, following formation of $CaF_2$ by addition of $Ca(OH)_2$, is presented.

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## P2.54

# Fluoropolymers with enhanced dielectric properties through microlayer coextrusion

**M. MACKEY [a], Z. ZHENG [a], J. CARR [a], L. FLANDIN [b]*, E. BAER [a]**

[a] CLIPS, Case Western Reserve University - CLEVELAND (USA)
[b] LEPMI - UNIVERSITE DE SAVOIE, UMR 5279 - LE BOURGET-DU-LAC (FRANCE)

* Lionel.Flandin@univ-savoie.fr

Using coextrusion forced assembly**1** several fluoropolymers were processed with PC or PET to obtain films with 32- to 256- alternating layers. The materials showed improved dielectrics properties. Both low**2** and high**3** fields measurements demonstrated improvements over the corresponding monolith and commercial materials. The large enhancement arose from structural changes of the constituting polymers (confined crystallization, crystal orientation**3,4**) and from modifications in the conduction mechanisms of the fuoropolymers. Complementary electrical and structural investigations**5** lead to a plausible breakdown mechanism of layered structure that explains the dielectric strengths. The enabling technology provides a way to combine dissimilar polymers and permits the design of materials with unique properties. It was also successfully employed to tailor and improved optical, permeation and mechanical properties.

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## P2.55

# Supramolecular Complexes exploiting Fluorous-Fluorous Interaction

**W.J. DUNCANSON** [(a)], **M. ZIERINGER** [(a)], **O. WAGNER** [(b)]*

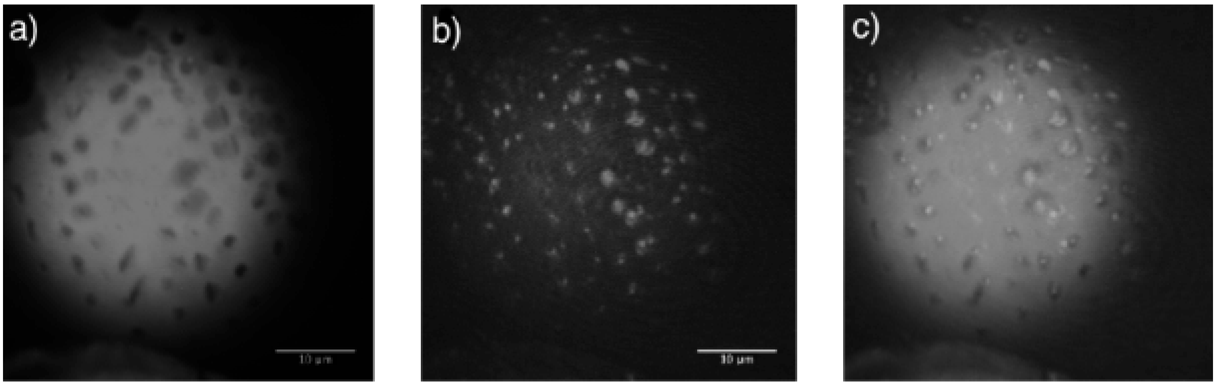
[(a)] Weitzlab - CAMBRIDGE (USA)
[(b)] FU BERLIN, ORGANIC CHEMISTRY - BERLIN (DEUTSCHLAND)

* olaf.wagner@fu-berlin.de

Fluorous interactions are being investigated as alternatives to traditional noncovalent interactions. This reversible "super-hydrophobic" interaction engendered by fluorous moieties provide a powerful driving force for self-assembly of these fluorous amphiphiles (*F*-amphiphiles) into films, membranes, micelles, vesicles and other stable supramolecular constructs.[2]

The presentation will be about the current approach to investigate the formation of supramolecular complexes by fluorous moieties. [3]

The stabilization of gas micron-sized bubbles of these complexes in solution, was used as a pore forming agent to create porous micro-spheres in a microfluidic system.



*Polylactide microsphere (red) with fluoro-functionlized pore surface (green); scale bar 10 µm*

**P2.56**

# The Road to Trifluoromethyl-containing Metallocene Carboxylic Acids

**M. MASCHKE** [(a)]*, **M. LIEB** [(b)], **N. METZLER-NOLTE** [(b)]

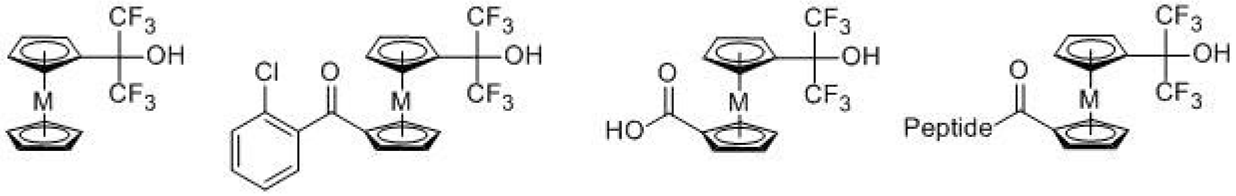
[(a)] RUHR-UNIVERSITY BOCHUM, CHAIR OF INORGANIC CHEMISTRY I - BIOINORGANIC CHEMISTRY - BOCHUM (GERMANY)
[(b)] RUHR-UNIVERSITY BOCHUM - BOCHUM (GERMANY)

* marcus.maschke@rub.de

In the last decades, bioinorganic chemistry has attracted much attention due to the development of therapeutic compounds against cancer, such as ferrocifen and ferroquine. Both highlight the possible medicinal applications of organometallic compounds.[1 - 4] However, widely used anti-cancer drugs such as cisplatin, are toxic due to their lack of selectivity. Nevertheless, worldwide, cancer patients are still treated with cisplatin. For this reason, new compounds have to be found which show higher selectivity, specific for cancer cells. Among the above mentioned therapeutic agents fluorinated species are nearly unknown. On the other hand, fluorinated compounds such as 5-fluorouracil or 5-fluorocytosine are among the oldest commercially available chemotherapeutic agents.

The introduction of the fluorinated substituents into the redoxactive metallocene scaffold poses a considerable challenge; direct introduction of trifluoromethyl groups often implies the use of strong oxidizing agents and acidic conditions. However, the $C(CF_3)_2OH$-function[5] (HFA) can easily be incorporated into the metallocene scaffold. Furthermore, nothing is known about the biological activity of these novel trifluoromethyl-substituted metallocenes.

Herein we report the synthesis and characterization of the compounds 1 - 4 . Incorporation of the strong electron withdrawing substituent influences the physicochemical properties, e.g. lipophilicity and electrochemistry, as well as the cytotoxic effect against cancer cells. Moreover, compound 4 can easily be synthesized via solid-phase peptide synthesis (SPPS). All compounds were checked for their antiproliferative effect, lipophilicity and electrochemical behavior.



**1** **2** **3** **4**

M = Fe, Ru

*Synthesized compounds 1 – 4.*

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[4] D. Dive, C. Biot, *ChemMedChem.*, **3** (2008) 383.
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**P2.57**

# Nucleophilic radiofluorination at room temperature via aziridiniums

**M. MEDOC [(a)], C. PERRIO [(a)*], F. SOBRIO [(a)]**

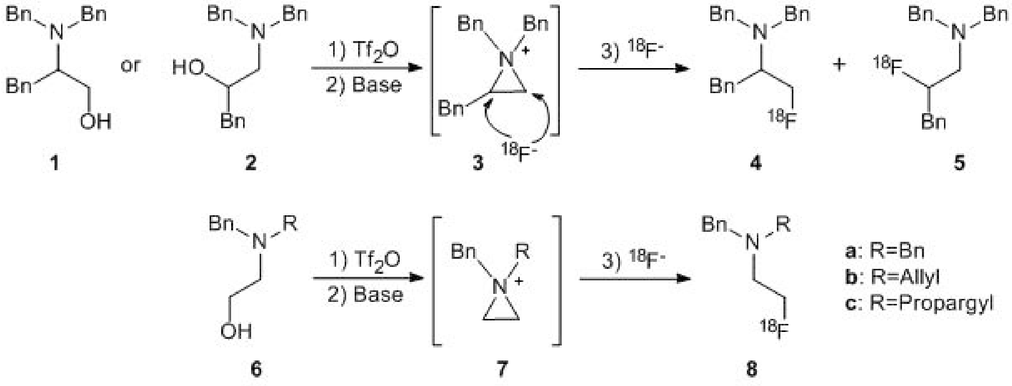
[(a)] LDM-TEP, UMR6301 ISTCT, CNRS, CEA, Unicaen, UMR 6301 ISTCT - LDM-TEP - CAEN (FRANCE)

* perrio@cyceron.fr

β-fluoroamine moieties are commonly present in bioactive molecules and are present in some PET radiotracers. However, electronics effects on amine can cause instability of the precursors (sulfonates or halides) leading to an unstable and very reactive aziridinium intermediate [1] and then involve a two-steps radiosynthesis including the synthesis of [$^{18}$F]-fluoroethylhalide followed by an alkylation reaction. The aziridiniums are well-known in synthetic chemistry and were used for fluorination using DAST or Deoxofluor [2,3]. Nevertheless, there are only a few examples of nucleophilic fluorination from aziridinium intermediates [4,5]. Here, based on *in situ* aziridinium formation from b-aminoalcohols, we have developed the nucleophilic radiolabelling of β-[$^{18}$F]fluoroamines in one radioactive step at room temperature.

The preparation of the aziridinium 3 starting from precursor 1 was developed studying the influences of the leaving group as well as the reaction conditions used. The isomers 4 and 5 were obtained in around 58% yield at room temperature in a 4/5 ratio about 1/2. The [$^{18}$F]-incorporation yield was determined by radioTLC and could be increased up to 83% at 90°C. The reaction mechanism involving the aziridinium reactive intermediate 3 was confirmed starting from the isomer precursor 2. Then, the best conditions were used for the radiolabelling of *N*-fluoroethyl substituted molecules 8a-c. Starting from the corresponding alcohol precursor 6a-c, the molecules 8a-c were obtained within 7 to 33% yields.

In conclusion, we have developed a new method for the nucleophilic [$^{18}$F]-radiolabelling of β-fluoroethylamines at room temperature by reaction with aziridinium intermediates. This method could be used for the preparation of radiopharmaceuticals containing the *N*-fluoroethyl moiety by a one-step radiosynthesis instead of a classical two-steps radiosynthesis.



*Synthesis of [18F]-isomers 4 and 5 and N-[18F]-2-fluoroethyl compounds 8 from aziridinium intermediates.*

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P2.58

# Complex Processing of Wastes Containing Fluorine

**P. GORDIENKO [(a)], G. KRYSENKO [(a)], S. IARUSOVA [(b)]*, E. PASHNINA [(a)], V.I. KHARCHENKO [(c)]**

[(a)] Institute of Chemistry, FEB RAS - VLADIVOSTOK (RUSSIAN FEDERATION)
[(b)] Institute of Chemistry, FEB RAS, LAB OF PROTECTING COATINGS AND MARINE CORROSION - VLADIVOSTOK (RUSSIAN FEDERATION)
[(c)] Institute of Chemistry, FEB RAS, LABORATORY OF ESQCS - VLADIVOSTOK (RUSSIA)

* yarusova_10@mail.ru

The work presents the research results of complex processing of industrial wastes containing fluoride at the Yaroslavskiy mining and enrichment plant in order to extract fluorine and alkali metals in a soluble form.

Treatment of the wastes of fluorite flotation was performed by the concentrated sulfuric acid at presence of silica simultaneously with removing of fluorine and silicon from the studied material in a form of the volatile silicon tetrafluoride. Silicon tetrafluoride was caught by the 15% solution of $NH_4F$, followed by hydrolysis of the resulting ammonium hexafluorosilicate by ammonia. In the hydrolysis of ammonium hexafluorosilicate, the ammonium fluoride and amorphous silica gel was obtained.

It was found that the highest fluorine extraction is achieved at the stoichiometric ratio of $CaF_2$ and silica. Taking into account the obtained results, $CaF_2$ was added for complete decomposition of the studied mineral raw material. The amount of $CaF_2$ was calculated by the fluoride ion and content of calcium fluoride in the sample.

Kinetic studies showed that under the sulfuric acid decomposition of wastes the maximal extraction of fluorine was achieved in 1.5 hours and was equal 65%. The maximal extraction of fluorine from the waste mixture with $CaF_2$ was achieved in 1 hour and was 82%.

To extract alkali metals, the mass formed as a result of the decomposition by sulfuric acid was treated with water and filtered. According to XRD, in the filtrate there were sulfates of aluminum, calcium, magnesium, iron, zinc and alkali metals.

The performed research showed that the sulfuric acid treatment of wastes of fluorite flotation with adding of the stoichiometric amount of $CaF_2$ makes it possible to extract alkali metals into a solution. Then they can be removed from the solution in a form of salts or hydroxides after separation and enriching by the ordinary technology.

Thus, the developed technological scheme of the sulfuric acid processing of raw materials containing fluorite allows bypassing the enriching step to perform the complex processing of raw materials containing fluorite and wastes of the fluorite flotation. The scheme provides a production of fluorinating agents, fluoride ammonium and hydrodifluoride ammonium, an extraction of alkali metals in a form of soluble sulfates, and a processing of by-products into environmentally safe materials of great demand.

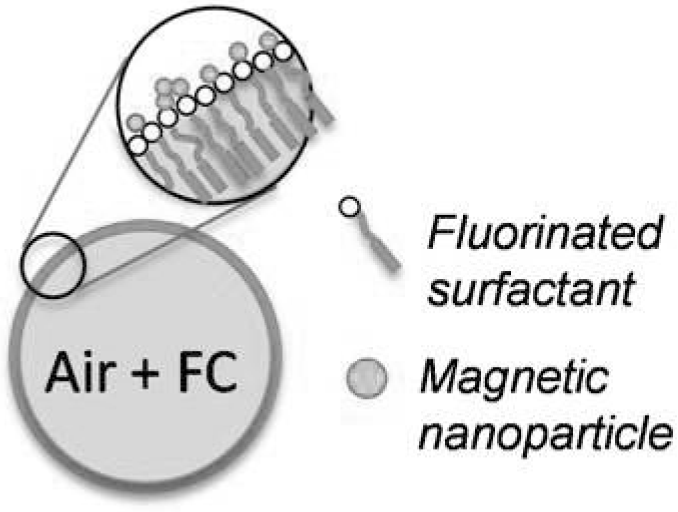
## P2.59

# Perfluoroalkylated Amphiphiles as Key Components for the Engineering of Compressible Multi-Scale Magnetic Constructs

**P.N. NGUYEN [a], G. NIKOLOVA [a], P. POLAVARAPU [a], G. WATON [a], G. POURROY [b], L.T. PHUOC [b], M.P. KRAFFT [a]***

[a] Institut Charles Sadron (CNRS) University of Strasbourg - STRASBOURG (FRANCE)
[b] IPCMS University of Strasbourg - STRASBOURG (FRANCE)

* krafft@unistra.fr



New multi-scale hybrid organic/inorganic constructs consisting of small gas microbubbles (1-5 µm) decorated with magnetic $Fe_3O_4$ or $CoFe_2O_4$ nanoparticles (NPs, 10 or 20 nm) in suspension in aqueous media have been engineered and characterized.[1] We have exploited our recent discovery that exceptionally stable microbubbles can be obtained by using (perfluoroalkyl)alkyl phosphates $C_nF_{2n+1}(CH_2)_mOP(O)(OH)_2$ (n = 6 and 8; m = 2, 5, 11; FnHmPhos) to form the bubbles' wall and a fluorocarbon gas (*F*-hexane) as an osmotic stabilizer.[2-6] Both large (6 µm) and much smaller (0.8 µm) nanoparticle-decorated, narrowly-distributed bubble populations were isolated. The high echogenicity, characteristic of microbubbles coated with self-assembled small molecules, is not reduced by the grafting of nanoparticles, indicating that shell flexibility is preserved. The new magnetic microbubbles spontaneously align in the direction of a magnetic field. These constructs have potential as bimodal contrast agents for echosonography and magnetic resonance imaging (MRI) and for gene and drug delivery enhancement. Our true air/fluorocarbon gas microbubbles, which are enclosed within a thin and highly flexible fluid film, self-assembled from a perfluoroalkylated surfactant, are preferable to the previously reported polymeric capsules and oil microdroplets (lipospheres), as lesser sound dampening allows generation of a stronger ultrasound response

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## P2.60

# Synthesis of Precursors of Polyfluorinated NHC Ligands

**O. SIMUNEK** [(a)]*, **M. RYBACKOVA** [(a)], **J. KVICALA** [(a)]

[(a)] Department of Organic Chemistry, INSTITUTE OF CHEMICAL TECHNOLOGY, PRAGUE - PRAGUE 6 (CZECH REPUBLIC)

* ondrejsimunek@seznam.cz

*N*-Heterocyclic carbenes (NHC) are an important class of ligands for transition metals. Due to their unique electronic properties, Grubbs and Hoveyda-Grubbs catalysts for alkene metathesis are more stable and at the same time more active than those with phosphane ligands. Processes employing analogous catalysts bearing fluorous NHC ligands might benefit from the well established fluorous separation techniques. As was previously observed in our laboratory, NHC ligands derived from 1,3-disubstituted imidazolium salts carrying linear polyfluoroalkyl chains were not stable and therefore their ruthenium complexes could not be synthesized [1].

In this work we prepared unsymmetrical imidazolium salts with one aromatic and one polyfluoroalkyl substituent (Fig. 1). These salts were then used for the synthesis of transition metal complexes, e.g. silver, palladium or ruthenium. Moreover, the silver complexes were utilized in transmetalation reactions with other metals.

Another type of NHC ligand precursors is represented by symmetrical imidazolium salts bearing two branched polyfluoroalkyl chains. These can be synthesized from the corresponding polyfluorinated amines.

*This work was financially supported by the Grant Agency of the Czech Republic (grant No. 207/10/1533).*

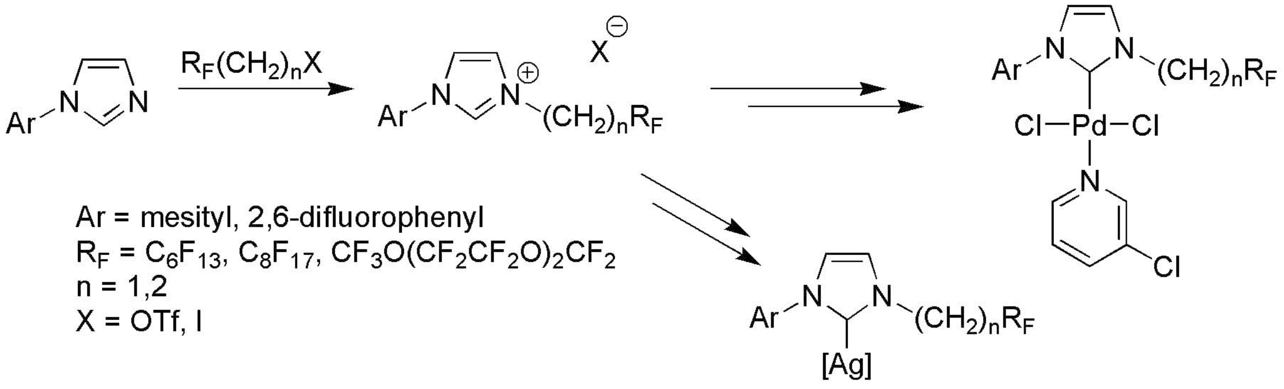

*Fig.1: Synthesis of unsymmetrical imidazolium salts.*

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**P2.61**

# Intermediates for NHC Ligands Substituted with Polyfluoroalkyl Chains in the Positions 4 and 5 of Imidazolidine Ring

**J. HOSEK** [(a)]*, **J. KVICALA** [(a)], **M. RYBACKOVA** [(a)]

[(a)] Department of Organic Chemistry, INSTITUTE OF CHEMICAL TECHNOLOGY, PRAGUE - PRAGUE 6 (CZECH REPUBLIC)

* hosekj@vscht.cz

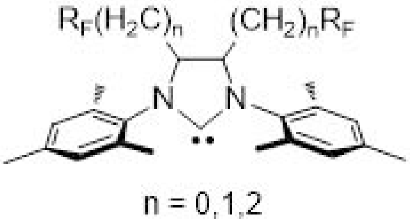

*Fig. 1 Target NHC ligands*

One of the objectives of our research group is the preparation of the analogues of 1st and 2nd generation Grubbs and Hoveyda-Grubbs catalysts substituted with polyfluoroalkyl chains. Our main goal is to synthesize new complexes with higher or at least similar efficiency then commercially available catalysts, which possess heavy fluorous properties. We focused on the synthesis of intermediates of NHC ligands connected to positions 4 and 5 of imidazolidine ring with per- or polyfluoralkyl chains bearing optional non-fluorinated linker of various length (Fig. 1).

The synthesis of the NHC ligands with directly attached perfluoralkyl chain started from perfluoralkanoic acid. We first prepared the respective imidoyl chlorides followed by transformation into imidoyl iodides using Finkelstein reaction. In the next palladium catalyzed reaction, we coupled selected imidoyl iodides to form diimines[1]. Simplest diimine bearing trifluoromethyl chains was reduced to the corresponding diamine. However, all attemps to prepare the NHC ligands from this diimine failed.

In the attempted synthesis of ligands containing methylene spacer between the perfluoroalkyl chain and imidazolidine ring, we started from 7H,7H,10H,10H-perfluorohexadecane-8,9-diol [2], which we oxidized to the respective diketone. Due to high acidity of hydrogens in the α-positions of diketone, undesired elimination of HF took place and this synthesis was abandoned.

Analogous synthetic pathway using vicinal diketone was chosen for the NHC ligand with perfluoroalkyl chain connected through ethylene spacer. In the first variant of the synthesis, we prepared the starting diketone by low temperature acyloin condensation of methyl 2H,2H,3H,3H-pefluorononanoate followed by oxidation of the acyloin, or directly using polyfluoroalkylated organometals and oxalic acid derivatives. However, the preparation of diimine from vicinal diketone was again unsuccesful. We finally succeeded in the synthesis of the target diamine using addition of polyfluoroalkyllithium on N,N'-disubstituted diimine. Subsequent formation of dihydroimidazolium salt proceeded in excellent yield.

This work was financially supported by the Grant Agency of the Czech Republic (grant No. 207/10/1533).

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## P2.62

# Guest-Adjusted Encapsulations by Cu(II) Coordination Complexes through Electrostatic Interactions Induced by Fluorine Substitutions

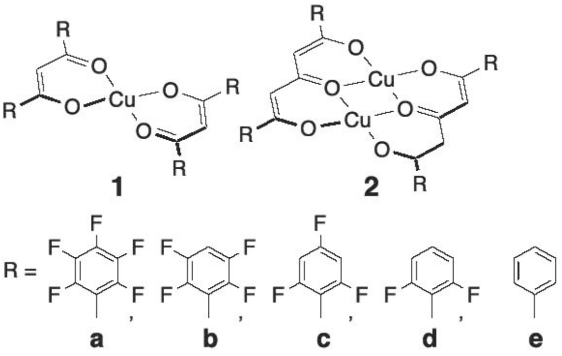
**A. HORI** [(a)]*, **K. NAKAJIMA** [(b)], **S. SAKAI** [(b)], **H. YUGE** [(b)]

[(a)] KITASATO UNIVERSITY, DEPARTMENT OF CHEMISTRY, SCHOOL OF SCIENCE - SAGAMIHARA-SHI (JAPAN)
[(b)] KITASATO UNIVERSITY - SAGAMIHARA-SHI (JAPAN)

* hori@kitasato-u.ac.jp

Current importance of the research for adsorption materials with solid-state host frameworks has focused on the creation of dynamic structural exchanges and selective guest recognitions. Herein we report the flexible host frameworks of mono and dinuclear coordination complexes, which were designed and encapsulated several organic guest molecules through electrostatic interactions in their crystals, in which the unique guest recognitions and the uniform cavities were induced by fluorination of the coordination complexes.

The crystals of the fully fluorinated coordination complexes, 1a [ref. 1] and 2a, achieved several guest encapsulations (Table 1), *e.g.*, benzene, xylenes, mesitylene, durene, anisole, m-dimethoxy-benzene, etc. Based on the crystallographic studies of these crystals, the axial positions on the metal ion and the surrounding spaces by the pentafluorophenyl groups produced the flexible cavity, and the guest molecules were recognized by cooperative effects of the metal···π, CF···H, and arene-perfluoroarene interactions. On the other hand, the guest-recognition of partially fluorinated coordination complexes, in which the pentafluorophenyl groups of 1a were replaced by 2,3,5,6-tetrafluorophenyl (1b), 2,4,6-trifluorophenyl (1c), 2,6-difluorophenyl (1d), and phenyl (1e) groups, clearly depended on the fluorination numbers, *e.g.*, the number of encapsulated benzene molecules is 3 (1a) > 2 (1b and 1c) > 0 (1d and 1e).



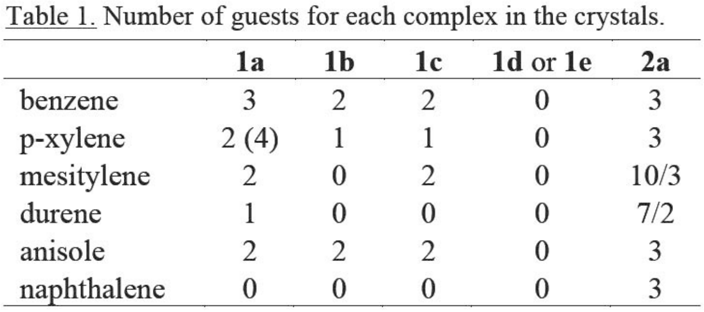


Table 1. Number of guests for each complex in the crystals.

| | 1a | 1b | 1c | 1d or 1e | 2a |
|---|---|---|---|---|---|
| benzene | 3 | 2 | 2 | 0 | 3 |
| p-xylene | 2 (4) | 1 | 1 | 0 | 3 |
| mesitylene | 2 | 0 | 2 | 0 | 10/3 |
| durene | 1 | 0 | 0 | 0 | 7/2 |
| anisole | 2 | 2 | 2 | 0 | 3 |
| naphthalene | 0 | 0 | 0 | 0 | 3 |

No encapsulation was observed with any guest molecules for 1d, although cavity spaces similar to 1a-c are present around the axial position on the metal by steric hindrance of the ortho-substituted fluorines, indicating the importance of more than three fluorine substitutions. In the crystallization processes, naphthalene molecules are inserted in the cavity of 2a to give single crystals of 2a•(naphtha-lene)$_3$, while no host-guest interactions were observed for 1a. It is pointed out that the cavity space on the metal of 2a is sufficient for naphthalene, producing the heterogeneous guest encapsulation to give 2a•(benzene)$_2$ •(naphthalene).

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## P2.63

# Interaction of fluorohalogenates of alkali and alkali-earth metals with arenediazonium tosylates, nitrobenzene and styrene.

**V. SOBOLEV [(a)] , V. RADCHENKO [(b)], R. OSTVALD [(b)]*, I. GERIN [(b)], V. FILIMONOV [(b)]**

[(a)] TOMSK POLYTECHNIC UNIVERSITY, FLUORINE CHEMISTRY AND ENGINEERING - TOMSK (RUSSIA)
[(b)] TOMSK POLYTECHNIC UNIVERSITY - TOMSK (RUSSIA)

* vsobolev1989@tpu.ru

For the first time the reactions of interaction between tetraflourobromates (III) of alkali and alkali-earth metals and arenediazonium tosylates, nitrobenzene and styrene were researched. The extremely high reactivity of fluorobromates (III) with mentioned organic compounds was found. The products of interaction were identified by a GC-MS method. Various brominated and fewer fluorinated moieties were found. This result makes promising further investigations of the properties of these compounds as reagents for organic synthesis.

Tetrafluorobromates of barium and potassium demonstrate the extremely high reactivity with mentioned organic compounds. In case of interaction of Ba(BrF4)2 and KBrF4 with arenediazonium tosylates the reaction of tosylates decomposition with obtaining of electrophilic substitution product and electrophilic bromination occurs. The process with nitrobenzene is extremely selective, in comparison with previous one. The only product of interaction is 3-bromo-nitrobenzene. This result is completely consistent with the S.Rozen paper [1], where the interaction of BrF3 and nitrobenzene was researched. The GC-MS data for this experiment are shown at Fig. 1. Reaction with styrene is not so selective, but the GC-MS data have shown us that the processes of double-bond bromination and aromatic core fluorination occurred. More results and discussion are shown in the full-paper of this research [2].

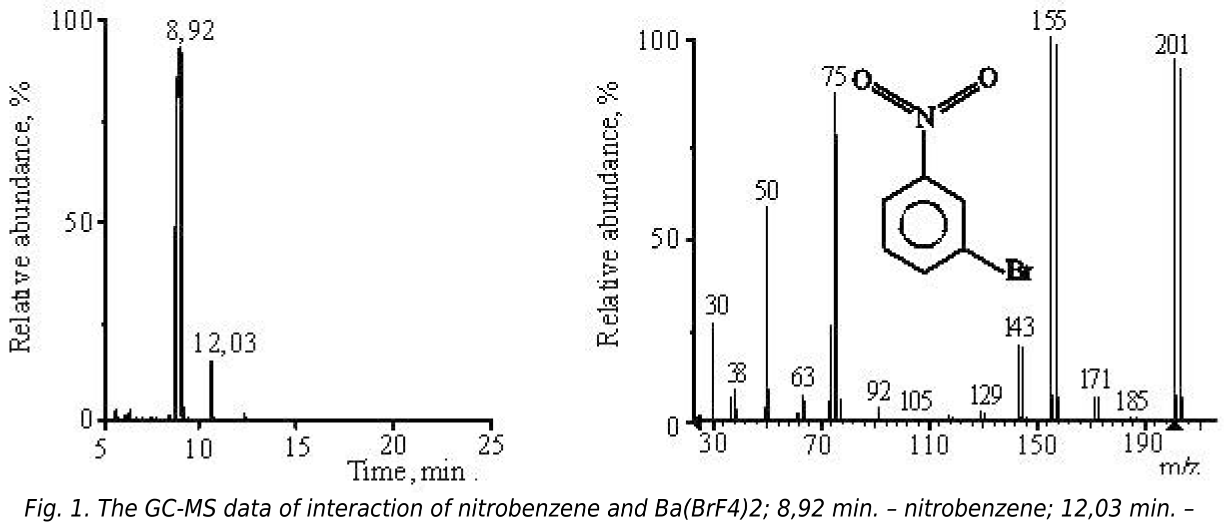

*Fig. 1. The GC-MS data of interaction of nitrobenzene and Ba(BrF4)2; 8,92 min. – nitrobenzene; 12,03 min. – 3-bromonitrobenzene;*

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## P2.64

# Water treatment after firefighting foam uses: Implementation at real scale

**R. SEVERAC [b] , M. PABON [c]*, C. BAUDEQUIN [a], E. COUALLIER [a], M. RAKIB [a]**

[a] Laboratoire de Génie des Procédés et matériaux, École Centrale Paris, - CHÂTENAY-MALABRY (FRANCE)
[b] DUPONT DE NEMOURS SAS - MANTES LA VILLE (FRANCE)
[c] DUPONT DE NEMOURS INTERNATIONAL - GENEVA (SWITZERLAND)

* martial.pabon@dupont.com

Fluorotelomer-based surfactants have been produced and used since the 1970’s because of their unique chemical-physical properties. Specifically, they have unique surface-tension lowering capability in aqueous systems at low concentrations, e.g. 100’s of ppm. Compared to hydrocarbon surfactants, fluorotelomer-based surfactants have a lower critical micelle concentration. The surface tension of water is reduced from 72 to 16 $mN.m^{-1}$ at 25°C whereas classical surfactants lead only to 30 $mN.m^{-1}$. These specific properties make them highly suitable for many industrial processes which require low surface energy solutions such as aqueous firefighting foam (AFFF).

Extinguishments of large scale solvent fires produce large amounts of water that may contain various fluorinated surfactants depending on the type of firefighting foam used. Due to their chemical nature, fluorinated parts of fluorinated compounds are highly resistant to biochemical and advanced oxidation processes. Therefore the current treatment for the degradation of fluorinated surfactant from water used in fire extinguishment is high temperature incineration of the water in halogen resistant incinerators. This work aims to propose a process for purifying firefighting water containing fluorinated surfactants combining electrocoagulation with reverse osmosis.

Examples of existing equipment will be presented that illustrate the interest and the reality of such treating units.

## P2.65

# Fluorination study mechanism on various porous carbon materials

**C. GHIMBEU [(a)], K. GUERIN [(b)*], J. DENZER [(a)], M. DUBOIS [(c)], C. VIX-GUTERL [(a)]**

[(a)] Institut de Science des Matériaux de Mulhouse, CNRS LRC 7228 - MULHOUSE (FRANCE)
[(b)] Institut de Chimie de Clermont-Ferrand - AUBIERE CEDEX (FRANCE)
[(c)] Université blaise pascal - AUBIERE (FRANCE)

* katia.guerin@univ-bpclermont.fr

In order to understand the fluorination mechanism of a variety of ordered and disordered porous carbons, the influence of the fluorination conditions on the physicochemical characteristics and adsorption properties were studied in this work by several techniques(nitrogen adsorption, TEM, XRD, XPS, IR and Raman spectroscopies, TPD-MS, solid state NMR with 13C and 19F nuclei). It was for the first time that the temperature programmed desorption coupled with mass spectrometry technique was used to determine the surface chemistry of such carbon fluoride materials and the strength of the C-F bonds. Four types of carbons were synthesised: two Carbide-Derived Carbons (CDCs), two ordered carbons (SBA-15 silica and zeolite beta replica). These were compared with a commercial activated carbon. Several experimental fluorination conditions were performed: molecular fluorination with pure gaseous fluorine in static and dynamic conditions and atomic fluorination generated by xenon difluoride decomposition. Thus, these treatments allowed to control the F/C atomic ratio. For all the fluorinated carbons, the fluorination level was correlated with the fluorine reactivity. We showed that the highest fluorination level is achieved in static conditions compared to the dynamic conditions while the lowest reactivity is obtained with the atomic fluorine conditions. For the same fluorination condition, the C-F bonding is strongly dependent on the physical-chemical characteristics of porous carbon. The carbon replicas are very reactive towards fluorination compared to the CDCs and the activated carbon as underlined by the presence of CFx bonds (NMR and TPD-MS measurements). The carbon textural and structural properties and also its surface chemistry are strongly modified by the fluorination conditions. The carbon modification characteristics with the fluorination conditions will be basically discussed in this paper. The present work allows to understand the fluorination of porous carbons and moreover to select the most suitable fluorination conditions in regard of a specific potential application of these fluorinated carbon materials.

## P2.66

# Fluorinated carbon derived carbide as electrode material in supercapacitors

**K. GUERIN [a]*, C. AYINGONE MEZUI [a], N. BATISSE [a], L. FREZET [a], M. DUBOIS [a], B. DAFFOS [b], P. SIMON [b], C. GHIMBEU [c]**

[a] Institut de Chimie de Clermont-Ferrand - AUBIERE CEDEX (FRANCE)
[b] CIRIMAT-LCMIE, Université Paul Sabatier - TOULOUSE (FRANCE)
[c] Institut de Science des Matériaux de Mulhouse, CNRS LRC 7228 - MULHOUSE (FRANCE)

* katia.guerin@univ-bpclermont.fr

Since a decade, a new way to produce nanoporous carbons consists in chlorination of metal carbide in order to etch metallic atoms and to leave the carbon matrix. Gaseous molecular chlorine reacts with metallic atoms at high temperature (600 – 900°C) to form most of the time a gaseous chloride (which is easily removed) and carbon called carbide derived carbon (CDC). The unique nanoporous structure of CDC together with a narrow pore size distribution and possibility to tune the pore size distribution has noticeably forced the development of applications requiring nanoporous materials such as fuel cells, adsorption processes, hydrogen storage... One of the most challenging applications is the rapidly developing field of the electrochemical energy storage devices such as super- or ultracapacitors. Up to now, the best CDC materials for supercapacitors have been made by chlorination of titanium and silicon carbides. In order to enhance the diffusion of electrolyte anion, a complementary fluorination post-treatment can be efficient. In this study, 3 different fluorination ways were conducted on CDCs obtained from chlorination of 2H and 3C silicon carbide: static fluorination with pure fluorine gas, dynamic fluorination with pure fluorine gas and controlled fluorination by atomic fluorine formed in situ by thermal decomposition of $TbF_4$. All the fluorinated CDCs have been characterized by Temperature Programmed Desorption coupled with mass spectrometry (TPD-MS), X-ray diffraction, solid state nuclear magnetic resonance, infra-red and Raman spectroscopy in order to determine the nature and the strength of the C-F bonding. The fluorination mechanism differs owing to the 3 fluorination ways and has a direct consequence on the porous distribution. The performances of all the fluorinated CDCs as electrode material in supercapacitors were investigated by cyclic voltammetry and electrochemical impedance spectroscopy in organic electrolytes.

## P2.67

# Characterization of polymer multilayer for photovoltaic application with Infrared and Raman microscopy

**E. PLANES [(a)], B. YRIEIX [(b)], L. FLANDIN [(a)]***

[(a)] LEPMI, UMR 5279, CNRS ; Grenoble INP – Université de Savoie, Université J. Fourier ; LMOPS INES - LE BOURGET-DU-LAC (FRANCE)
[(b)] EDF, R&D Matériaux et Mécanique des Composants - MORET-SUR-LOING (FRANCE)

* Lionel.Flandin@univ-savoie.fr

Infrared and Raman microscopy are powerful tools to analyze the degradation of encapsulation systems of PV modules. In this communication, the study is devoted to the encapsulant materials of a flexible PV panel. Different characterizations techniques (optical microscopy, infrared spectroscopy, infrared and Raman microscopy, DSC, TGA) were first employed to characterize the structure of the encapsulation system: the number and nature of different layers were determined. The encapsulation system was then characterized after accelerated ageing at 80°C/85% RH for 2000h. The consequences of this ageing were more specifically studied by infrared and Raman microscopy. These two techniques are found to furnish valuable results for the photovoltaic application. A significant loss in fluorine content as a function of the sample thickness was evidenced in the ETFE layer after ageing. Complementary tools were also tested, that lead to results very sensitive to the sample preparation. A comparison of the entire series of methods will be presented. In conclusion specific properties in agreement will be shown related to the application (optical) as well as their changes as a function of ageing time.

## P2.68

# Fluorinated diketones – A selective passivation for highly stable electronic devices

**N. KALINOVICH [a]*, M. ORTEL [a], Y. TROSTYANSKAYA [a], V. WAGNER [a], G.V. ROESCHENTHALER [a]**

[a] JACOBS UNIVERSITY BREMEN GGMBH, SCHOOL OF ENGINEERING AND SCIENCE - BREMEN (GERMANY)

* n.kalinovich@jacobs-university.de

Metal oxide semiconductors like ZnO, $In_2O_3$ and IGZO (Indium Gallium Zink Oxide) are promising candidates for next generation electronics in smart and flexible electrical applications. Besides their high electrical performance and transparency these materials are suitable for cheap, wet-chemical production technologies e.g. printing. A major scientific challenge in this field is the understanding and improvement of the long term electrical stability in metal oxide devices, e.g. transistors.

In this work we report on selective chemical reactions at the surface of zinc oxide layers which were utilized to identify and passivate electrically active surface sites causing device instability. Therefore fluorinated diketones, i.e. hexafluoroacetylacetone, 4,4,4-trifluoro-1-phenylbutane-1,3-dione and 4,4,4-trifluoro-1(-3-fluorophenyl), were deposited from the gaseous phase on a zinc oxide surface which was deposited by spray pyrolysis. This type of compound is known to chelate selectively with $Zn^{2+}$-ions. The fluorination of the deposited compound greatly reduces the negative impact of ambient water on the electrical device characteristics.

The complex formation at the zinc oxide surface with the fluorinated diketones were monitored by contact angle measurements, morphological and optical characterisation techniques. These results were found to be in good agreement with electrical investigations which were conducted on thin film transistors (TFTs). Highly stable transistor characteristics were obtained after very short deposition time of the diketones (1s-60s). Passivated TFTs were still stable even after hours of operation. Furthermore the electrical device characteristics were found to improve, i.e. the charge carrier mobility values by up to 44% from $5.9 cm^2V^{-1}s^{-1}$ to $8.6 cm^2V^{-1}s^{-1}$ and the transistor on-set voltage moved close to the ideal value of 0V. We conclude that $Zn^{2+}$ on the surface is responsible for the creation of electrically active states which were successfully passivated by selective binding to fluorinated diketones. Moreover the increase in hydrophobicity of the ZnO surface reduces the sensibility of the device towards water significantly.[1]

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## P2.69

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# New cell for electrical conductivity measurements in molten fluorides

A. ROLLET [(a)]*, J. GOMES [(a)], H. GROULT [(a)]

[(a)] LABORATOIRE PECSA, UPMC - CNRS UMR 7195 - PARIS (FRANCE)

* anne-laure.rollet@upmc.fr

Molten fluorides are a particular class of liquids because all the components are ionic. Moreover, depending on the nature of the cations, the liquid structure may switch from a simple bath of charged hard spheres to a liquid network or a liquid with free complexes [1]. In addition to the fundamentals aspects, molten fluorides are used in numerous applications such as fluorine production [2], aluminium electrolysis [3], pyrochemical treatment of nuclear waste [4], generation IV nuclear reactors [5]. Nevertheless, the physical-chemical data concerning molten fluorides such as self-diffusion, viscosity, thermal and electrical conductivity are still scarce and dispersed because of the experimental hindrances to deal with: corrosiveness, temperature (300-1500°C), volativility... Most of the data concerning rare earth and actinide fluorides have been provided by Oak Ridge National Laboratory during the running of the Molten Salt Reactor.Although electrical conductivity has commonly been measured in molten chlorides, less data are available in molten fluorides [6]. Indeed, these experiments are very difficult to set up because of the important reactivity of these melts towards oxide glasses. Several designs of conductivity cell have been proposed [7,8]. Nevertheless, they require high amount of salt; in addition, they use only two electrodes while for highly conductive liquids a four electrodes setup is preferred. New materials are now commercially available that make it possible to design new cells and even new experiments as demonstrated for instance by recent High Temperature NMR for liquid structure and self-diffusion coefficient determination.[9] For molten fluorides, these materials are boron nitride without oxide binder, pyrolitic boron nitride and glassy carbon. In this poster, we will present a new design for electrical conductivity measurement in molten fluorides based on four-electrodes setup and requiring few grams of salt.

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## P2.70

# Sorption technologies processing of fluorinated gases in the nuclear industry

**A. BYKOV [a]*, O. GROMOV [a], V.A. SEREDENKO [a], R.L. MAZUR [b], A.V. SIGAYLO [b], J.B. TORGUNAKOV [b]**

[a] JSC 'Scientific-Research Institute of Chemical Technology', DEP. OF THE NUCLEAR MATERIALS - MOSCOW (RUSSIA)
[b] OJSC 'Sibirsky khimichesky kombinat' - SEVERSK (RUSSIA)

* bykovaa1@gmail.com

Elemental fluorine is one of the most active chemicals. It forms compounds with almost all chemical elements [1]. Fluorine ion is an universal cellular poison, its compounds actively interact with natural objects, disrupting the natural balance in these substances [2]. That's why it’s important and necessary to capture and neutralize of fluorine and its compounds.

Different gaseous products (other than $UF_6$) are formed during operation of the enrichment facilities, such as gases generated during standard operations with different tanks, containing uranium hexafluoride or pumping gaseous products collector of the condensation-evaporation plant. There are also gaseous products containing elemental fluorine, chlorine trifluoride and its decomposition products, hydrogen fluoride; their use for uranium hexafluoride production and technological equipment enrichment facilities. Sorption technologies are most efficient and cost-effective method for processing gaseous products forming work of the enrichment facilities. The advantage of using sorption technologies (for example, fluoride sorbents) for receive $UF_6$ from gaseous product is an opportunity to send $UF_6$ directly into the main technological process flow of the plant. Another advantage is the ability to fine cleaning waste gases up to values comparable with the sanitary standards of emissions.

This problem is successfully solved in the Isotope separation plant of the JSC «SChI» under the supervision specialists of JSC «Scientific-Research Institute of Chemical Technology». With the factory settings of the sorption process gas is recovered about 250 kg of $UF_6$, and about 300 kg of HF. For the first time in Russia’s nuclear industry reached cleaning waste gases at the maximum allowable concentration, and not at the level of maximum permissible emissions to be determined specifically for each company [3]. It is important to note that under the continuous rise prices for fluorite concentrates obtaining anhydrous hydrogen fluoride from gaseous products increases the profitability of production of JSC " SChI " and, in addition, increases the sustainability of the enterprise. Equipment such systems facilities nuclear fuel cycle in Russia, and similar enterprises of foreign countries, will significantly reduce pollution.

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## P2.71

# Perfluoropolyethers as hydrophobizing agents for Fuel Cells carbonaceous functional materials

**M. GOLA** [a]*, **W. NAVARRINI** [a], **M. SANSOTERA** [a], **C. BIANCHI** [b], **G. DOTELLI** [c], **P. GALLO STAMPINO** [c]

[a] POLITECNICO DI MILANO, FLUORITECH - MILANO (ITALIA)
[b] UNIVERSITA DEGLI STUDI DI MILANO - MILANO (ITALIA)
[c] POLITECNICO DI MILANO - MILANO (ITALIA)

* massimo.gola@chem.polimi.it

*Fig. 1 Water droplet on the superhydrophobic surface of a PFPE functionalized CC*

Linear perfluoropolyether (PFPE) peroxide has been used to functionalize conductive carbon black (CB) and carbon cloth (CC), to confer superhydrophobic properties to these substrates. The thermal decomposition of a linear PFPE peroxide produced linear PFPE radicals that covalently bonded the unsaturated moieties on the surface of CB and CC. Perfluorinated radicals can directly bond to the carbonaceous structure without any spacer that could decrease both thermal and chemical stability of the resulting materials [1]. Resulting material hydrophobicity has been verified by contact angle measurements, that demonstrated that water droplets were enduringly stable on the treated materials and that contact angle values were significantly high, exceeding the superhydrophobicity threshold. The relationship between the linkage of fluorinated chains and the variations of surface physical-chemical properties were studied combining X-ray photoelectron spectroscopy (XPS), resistivity measurements, scanning electron microscopy (SEM) and surface area analysis with Brunauer-Emmett-Teller (BET) technique. Changes in conductive properties has been checked by resistivity measurements. Results  revealed that, despite insulating nature of PFPE, functionalized carbonaceous materials retained their conductive properties [2].  The PFPE-modified CC were tested in a single fuel cell at the lab scale. The cell testing was run at two temperatures (60°C and 80°C) with a relative humidity (RH) of the feeding gases of  80/100% and 60/100% Hydrogen/Air respectively. AC electrochemical impedance spectroscopy (EIS) of the running cell was also performed. The EIS spectra were recorded at OCV and from low to high current density (i.e. 0.17, 0.34, 0.52, 0.7 and 0.87 A/cm2). The experimental spectra were modelled with all in-series equivalent circuits comprising a resistance and two parallel constant phase/resistance sub-circuits.

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## P2.72

# Fluorinated malonamides as tools to investigate liquid/liquid extraction phenomena

**M. DUL** [(a)], **D. BOURGEOIS** [(a)*], **D. MEYER** [(a)]
[(a)] ICSM, LCPA - BAGNOLS SUR CÈZE (FRANCE)
* damien.bourgeois@cea.fr

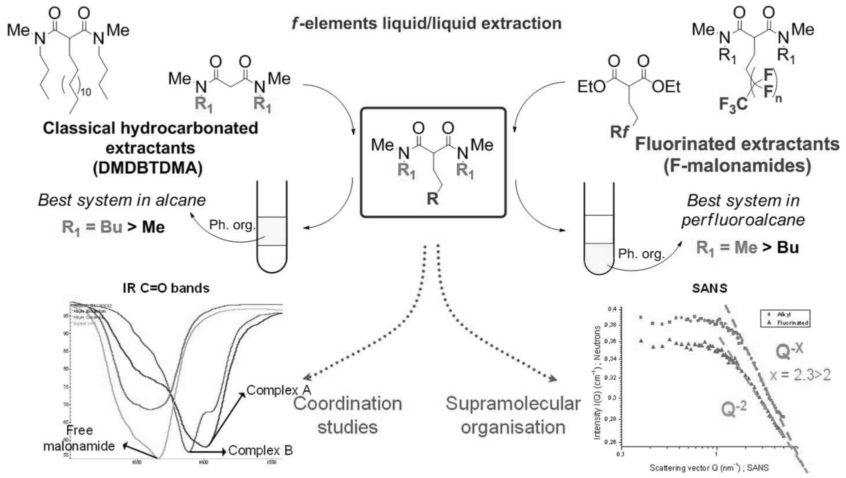


*Figure 1: F- and H-malonamides studied for L/L extraction*

Recovery of *f*-elements is a research subject of fast growing importance, with the need for efficient recycling of several rare earth metals, commonly used in optical, electronic, and magnetic devices. Amongst the different envisioned processes, hydrometallurgical ones are promising, since they are already well mastered for 1) pure rare earth production from different natural ores, and 2) partitioning of nuclear fuel fission products. In both cases, after digestion of solid matter with an acidic solution (hydrochloric, sulphuric or nitric), the metal cations are isolated from organic phases after liquid/liquid (L/L) extraction. Efficient extracting systems, based on amphiphilic molecules, were developed, but each system remains devoted to a particular input feed, with limited balance between constituents in the aqueous layer.

Malonamide ligands, with general formula $(MeR_1NCO)_2CHR_2$ (Fig. 1), are neutral amphiphilic molecules which have proved their potency for the extraction of *f*-elements and for the development of efficient processes for the retreatment of nuclear wastes, aimed at the lanthanide-actinide separation. Interestingly, as fluorous chemistry proved its efficiency in various fields including L/L extraction and purification of organic and inorganic compounds, no report to our knowledge deals to the adaptation of this technology for the separation of *f*-elements. Therefore, we prepared series of F-malonamides, and studied their behaviour during L/L extraction of various lanthanides, in different systems (organic, fluorous, Fig. 1). The structure-activity relationship of these extractants was established, with emphasis on the differences between hydrocarbon and fluorous systems.

Interestingly, in some conditions, we observe efficient neodymium extraction with the H-malonamide (DMDBTDMA), but no extraction with the corresponding F-malonamide (R1 = *n*Bu, n = 5, Fig. 1) with identical molecular volume. Thus, F-systems were methodically compared with the analogue H-systems. Coordination chemistry (IR, UV/vis, NMR) revealed similar molecular interactions, but physicochemical studies with small-angle X-ray and neutron scattering (SAXS, SANS) highlighted the essential role played by the supramolecular organisation of the organic phases during L/L extraction. All these results will be detailed and discussed.

## P2.73

# New cathode materials for Li-ion batteries based on HTB iron hydroxyfluoride $FeF_{3-x}(OH)_x$ $0.33H_2O$.

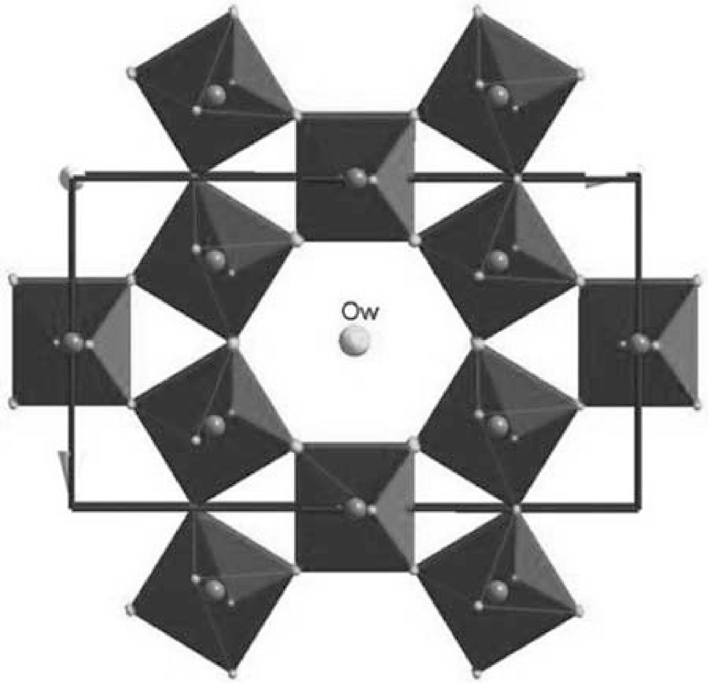
**M. DUTTINE** [(a)]*, **D. DAMBOURNET** [(a)], **H. GROULT** [(a)], **A. WATTIAUX** [(b)], **E. DURAND** [(b)], **K. CHAPMAN** [(c)],
**P. CHUPAS** [(c)], **C.M. JULIEN** [(a)], **K. ZHAGIB** [(d)], **A. DEMOURGUES** [(b)]

(a) LABORATOIRE PECSA, UPMC - CNRS UMR 7195 - PARIS (FRANCE)
(b) ICMCB-CNRS - PESSAC (FRANCE)
(c) ARGONNE NATIONAL LABORATORY - ARGONNE (USA)
(d) IREQ - VARENNES, QUEBEC (CANADA)

* mathieu.duttine@upmc.fr

Nowadays, cathode materials of most commercial lithium ion batteries are layered compounds based on $LiCoO_2$ network. But recently, olivine $LiFePO_4$ appeared to be a promising alternative for Li-ion or Li-metal cells due to a high theoretical capacity (170 mAh/g), its stability upon electrochemical reaction, and its low cost and toxicity. Moreover, iron fluoride $FeF_3$ exhibits a theoretical capacity of 237 mAh/g and a better stability than $LiFePO_4$ [1].

Iron trifluorides can adopt various networks including the $ReO_3$, the Pyrochlore or the Hexagonal-Tungsten-Bronze (HTB) type-structure [2]. The latter consists of corner-sharing $FeF_6$ octahedra forming hexagonal section along the c-axis (Fig. 1). Structural waters are located within the tunnels and can be thermally removed without any structural collapse [2].



*Representation of the HTB structure along the c-axis. Ow referred to structural water*

Well crystallized HTB iron trifluorides were prepared by microwave-assisted solvothermal routes with aqueous iron nitrate solution and HF as precursors (HF/Fe molar ration set to 2) [3]. Characterization of the as-synthesized compounds using MS-coupled TGA, FT-IR spectroscopy, XRD Rietveld and PDF analyses revealed the occurrence of structural OH groups ($F^-$ substituted by $OH^-$) leading to the chemical composition $FeF_{3-x}(OH)_x$ $0.33H_2O$ with x~0.8.

Annealing at various temperatures under Ar flow or in self-generated atmosphere led to HTB iron fluoride compounds with various oxygen contents including anionic vacancies or hydroxyl groups substituting for fluorine and different amounts of structural water. The electrochemical properties of these compounds as cathode materials in Li-ion batteries were investigated and show the strong impact of chemical composition, structural features and also crystallite size on electrochemical performance of HTB iron fluorides.

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## P2.74

# Molecular Dynamics Simulations of Supercapacitors: Determination of single-electrode capacitances, with complex electrode geometries

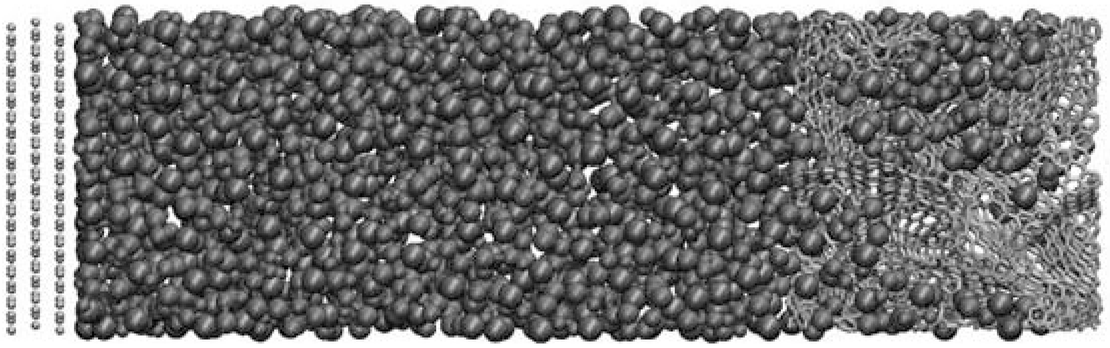
**C. PÉAN** [(a)(b)(c)]*, **M. SALANNE** [(a)(b)], **C. MERLET** [(a)(b)], **B. ROTENBERG** [(a)(b)], **P. SIMON** [(b)(c)]

[(a)] UPMC, Université Paris 06, CNRS, UMR 7195, PECSA - PARIS (FRANCE)
[(b)] Réseau sur le Stockage Electrochimique de l'Energie (RS2E) - FR CNRS 3459 (FRANCE)
[(c)] CIRIMAT-LCMIE, Université Paul Sabatier - TOULOUSE (FRANCE)

* clarisse.pean@upmc.fr

In this work we focus on electrical double-layer capacitors. We use classical molecular dynamics to simulate systems consisting in porous carbons as electrode material and the fluorinated ionic liquid [BMI][$PF_6$] as electrolyte. Our simulations are performed at constant potential, which corresponds to realistic conditions, unlike the case of constant electrode charge simulations [1].

Experimentally, it is possible to measure individually both capacitances of positive and negative electrodes, whereas in our simulations involving porous carbons we could up to now only determine the integral capacitance, calculated for the whole system [2]. Our aim is to calculate the capacitance of a single electrode. For this purpose, we take profit from the property of systems made of planar electrodes, in which the Poisson potential profile across the electrode/electrolyte interface can easily be calculated. We therefore construct a “hybrid” system involving one graphite electrode and one porous carbon electrode (see Figure). In this hybrid system, it is possible to calculate the potential of the bulk and use it as a reference to finally obtain the individual capacitance of each electrode. Our results are systematically compared to experimental values obtained for the same porous carbons.



*Typical simulation cell (green: [PF6] anions, red: [BMI] cations, cyan: carbon atoms). The left-end electrode is a planar graphitic carbon while the right-end one is a nanoporous carbon.*

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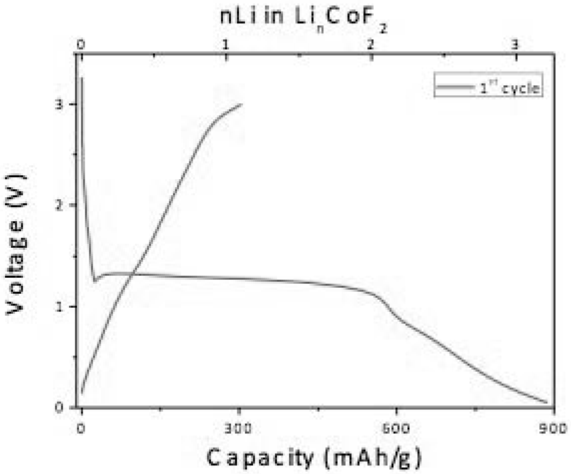
## P2.75

# Understanding Lithium Insertion Mechanism into $CoF_2$

**W. LI** (a)*, **D. DAMBOURNET** (a), **H. GROULT** (a), **K. CHAPMAN** (b), **P. CHUPAS** (b), **C. PEPIN** (c), **A. DEMOURGUES** (c), **M.L. DOUBLET** (d), **D. FLAHAULT** (e)

(a) Université Pierre et Marie Curie-Paris-6, Laboratoire des Electrolytes, Colloïdes et Systèmes Analytiques (PECSA) - PARIS (FRANCE)
(b) X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory - ARGONNE (USA)
(c) ICMCB-CNRS - PESSAC (FRANCE)
(d) Institut Charles GERHARDT, Chimie Théorique, Méthodologies, Modélisation, CNRS, Université Montpellier 2 - MONTPELLIER (FRANCE)
(e) Université de Pau et des Pays de l'Adour, IPREM-ECP, CNRS, UMR 5254 - PAU (FRANCE)

* wei.li@upmc.fr



*First cycle of Li/$CoF_2$ cell voltage profiles, cycled in a voltage window between 0.05-3V with a current density of 50 mA $g^{-1}$*

Owing to their characteristics, lithium ion batteries appeared to be one of the most promising devices for electrochemical energy storage applications. Depending on the nature of the electrode materials, three lithium storage mechanisms can be distinguished: lithium intercalation, alloying and conversion reaction. Materials that undergo conversion reaction allow more than one lithium per transition metal to be stored through the formation of metallic nanoparticles (2-3 nm) embedded in a lithiated matrix. However, mechanisms of conversion reaction are extremely complex due to drastic structural rearrangement along with the formation of nanoscaled or amorphous particles which are difficult to characterize. In this study, we report on the conversion mechanisms occurring in $CoF_{2.}$ Figure 1 shows the voltage profile of Li/$CoF_2$ cell cycled in a voltage window between 0.05-3V. In a conversion mechanism, the rutile network of $CoF_2$ should theoretically react with two lithium ions. Nevertheless, the discharge curve shown in Fig.1 revealed that $CoF_2$ reacted with 3.2 $Li^+$. Additionally, this reaction was shown be poorly reversible with a reaction of 1 $Li^+$. In order to describe the lithium storage mechanism occurring within $CoF_{2,}$ several methods were used. Therein we will present results from ex-situ x-ray Pair Distribution Function (PDF) analysis, x-ray photoelectron spectroscopy as well as first-principles calculations.

## P2.76

# Silica nanoparticles with bifunctional surface layers

**V. TOMINA [a]*, I. MELNYK [a], Y. ZUB [a]**

[a] CHUIKO INSTITUTE OF SURFACE CHEMISTRY NAS OF UKRAINE, SURFACE CHEMISTRY OF HYBRID MATERIALS - KYIV (UKRAINE)

* v.v.tomina@mail.ru

The present work was aimed to synthesize silica nanoparticles with bifunctional surface layers bearing both hydrophobic (fluorine-containing) and hydrophilic (nitrogen-containing) functional groups and suitable for the sorption of metals and biological substances. The syntheses were conducted using modified Stober method based on the reaction of hydrolytic co-polycondensation of trialkoxysilanes with tetraethoxysilane (TEOS) in ammonium hydroxide media [1].

Concerning hydrophobic functional groups, there were chosen fluorine-containing groups as possessing higher hydrophobic properties than alkyl groups; thus, 1H,1H,2H,2H- perfluorooctyltriethoxysilane (PFES) was used for functionalization. Hydrophobic groups in the surface layer influence the hydrogen bonds formation by the complexing groups, determining the structure of the complexes with metal ions. In addition they promote proteins and other organic molecules sorption due to the non-specific interaction [2].

Along with fluorine-containing groups there were also introduced hydrophilic amino-groups using 3-aminopropyltriethoxysilane (APTES) or N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPED) as functionalizing agents. Nitrogen-containing group proved effective in the removal of metal ions, such as $Ni^{2+}$ and $Cu^{2+}$ from aqueous environments. Thus, the combination of these two types of groups would enhance the sorption properties of the resulting materials.

The synthesized materials were studied using the variety of methods, including SEM, FTIR spectroscopy, thermogravimetry, gas adsorption, elemental analysis. Such materials feature nonporous particles of 100-400 nm in size and contain both types of functional groups, which was confirmed using FTIR spectroscopy.

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## P2.77

# Unpredictable and Perfect Synthesis of Fluorinated Cyclopentenones

**K. TARASENKO** [(a)], **O. BALABON** [(a)], **V. IVASYSHYN** [(a)], **G. HAUFE** [(b)], **I.I. GERUS** [(a)*], **V. KUKHAR** [(a)]

[(a)] Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science - KYIV (UKRAINE)
[(b)] Organisch-Chemisches Institut, Universität Münster - MÜNSTER (GERMANY)

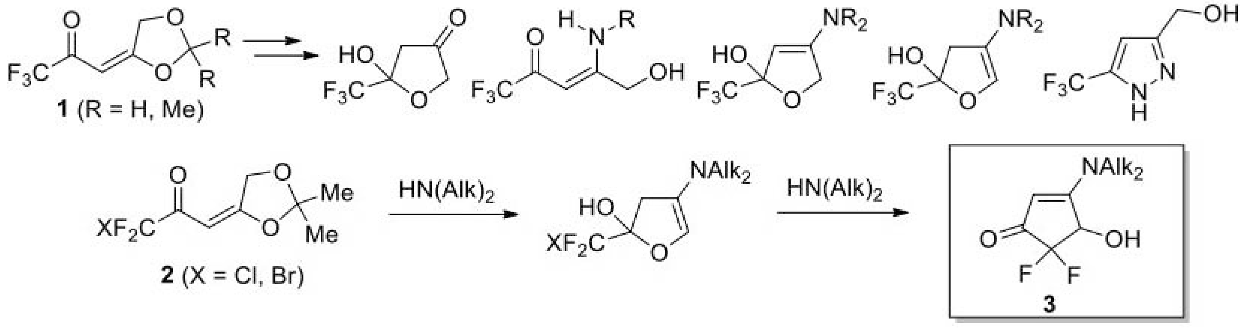
* igerus@hotmail.com

Readily available, reactive β-alkoxyvinyl polyfluoroalkyl ketones (enones) are widely used fluorinated building blocks for the synthesis of various polyfluoroalkyl containing heterocycles and natural product analogues. For recent examples see [1]. Recently, we developed a new type of cyclic enones 1 bearing an additional protected hydroxymethyl function [2]. Compounds 1 were utilized for various synthetic purposes, e.g. a series of $CF_3$ containing products was obtained.

Moreover, the cyclic enones 1 easily react with various *N*-nucleophiles at the β-position of the C=C double bond releasing a hydroxymethyl function, which adds to the C=O group to form a diversity of products. Unexpectedly, the reaction of $CClF_2$ or $CBrF_2$ containing cyclic enones 2 with secondary amines afforded 3-dialkylamino-5,5-difluoro-4-hydroxycyclopent-2-enones 3 in good isolated yield.

The *gem*-difluorocyclopentenones 3 are versatile intermediates to synthesize a wide variety of difluoromethylene analogues of biologically interesting compounds.

Syntheses and chemical particularities of the *gem*-difluorocyclopentenones 3 will be presented.



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## P2.78

# Direct Electrophilic Trifluoromethylation of Quinolones and Pyridones

**R. SENN** [(a)]*, **A. TOGNI** [(b)]

[(a)] ETH ZÜRICH, LABORATORY OF INORGANIC CHEMISTRY - ZÜRICH (SWITZERLAND)
[(b)] ETH ZÜRICH, DEPARTMENT OF CHEMISTRY - ZÜRICH (SWITZERLAND)

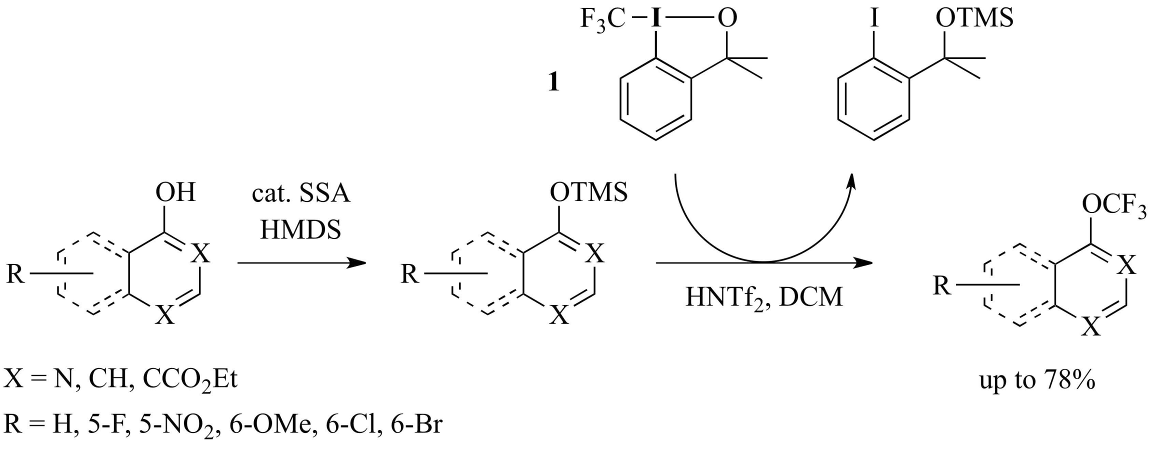
* senn@inorg.chem.ethz.ch

Since their discovery in the late 70's quinolone based antibiotics belong to the most prescribed broad-spectrum antibacterial drugs. [1] Especially compounds based on the fluoroquinolone core structure like Norfloxacin, Ciprofloxacin, Ofloxacin have found extensive application in treating various infectious diseases. [2]

Although a myriad of compounds were evaluated to further optimise their antibacterial activity and pharmacokinetic properties, N-trifluoromethylated fluoroquinolones still represent a rarity. [3] This is mainly due to the fact that the only known procedure to access such compounds relies on oxidative desulfurisation-fluorination. [4]

Recently, we reported the direct electrophilic *N*-trifluoromethylaton of a variety of nitrogen containing heterocycles, such as tetrazoles, triazoles, indazoles and pyrazoles [5] using the hypervalent iodine reagent 1, originally developed in our group. [6]

After *in situ* trimethylsilylation, similar conditions were examined with a variety of quinolones and pyridones, which were thus converted to the corresponding *O*-trifluoromethylated species in good yield and functional group tolerance. $^{19}$F- and $^{29}$Si-NMR 2D spectroscopy revealed that the silylation occurred exclusively at the oxygen atom, delivering some evidence for the observed selectivity of the trifluoromethylation.



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## P2.79

# Chemical State Analysis for Terbium Containing Oxide Fluoride Glasses Using Auger Electron Spectroscopy

**F. NISHIMURA** [(a)]*, **J. KIM** [(b)], **S. YONEZAWA** [(a)], **M. TAKASHIMA** [(b)]

[(a)] UNIVERSITY OF FUKUI, DEPT.MATERIALS SCI. & ENG. - FUKUI (JAPAN)
[(b)] UNIVERSITY OF FUKUI - FUKUI (JAPAN)

* fumihiro1986@gmail.com

The oxide fluoride glasses containing rare-earth elements have been prepared and characterized. It is important to know the chemical state of elements in the glass matrix to understand its functionality. In this study, AES (Auger electron spectroscopy) measurement was carried out to analyze the chemical sate of the elements in the glasses. Although it is usually difficult to analyze the glass sample having low electrical conductivity by using AES, it becomes possible to obtain the clear profile for the glass samples by the sample tilt method in this study.

The oxide fluoride glasses containing various amount of terbium ion were prepared and analyzed. The components of (70-x)$TbF_3$-20$BaF_2$-10$AlF_3$-x$GeO_2$ (mol%, x =30-60) were weighted and mixed in Ar. After drying the sample mixture under vacuum (less than 0.1 Pa) for 12 hours, it was compacted into Pt boat and set in an electric furnace filled with Ar. The mixture was melted at 1200 °C at the heating rate of 8 °Cmin$^{-1}$ in Ar. After holding at a certain temperature for 90 min, the melt was quenched. Products were analyzed by FL (fluorescent spectrometry), XRD, DSC, XPS and AES.

Fig.1(A) shows AES spectra (wide) of oxide fluoride glasses containing terbium. Since the fluorine content in the sample (a) was larger than the sample (b), the peak around 650 eV corresponded to fluorine in Fig.1(A) (a) appeared clearly compared to that in Fig.1(A) (b). Peaks observed between 850 and 1100 eV and around 1150 eV correspond to Tb and Ge, respectively. Fig.1(B) shows AES spectra of $Ba^{2+}$ in both glasses in their differential form. The peak at 595 eV for sample (a) was not observed for sample (b). That means the chemical state of $Ba^{2+}$ in sample (a) is different from that in sample (b). $Ba^{2+}$ may be sensitive to the change in the ratio between oxygen/fluorine in the glass matrices.

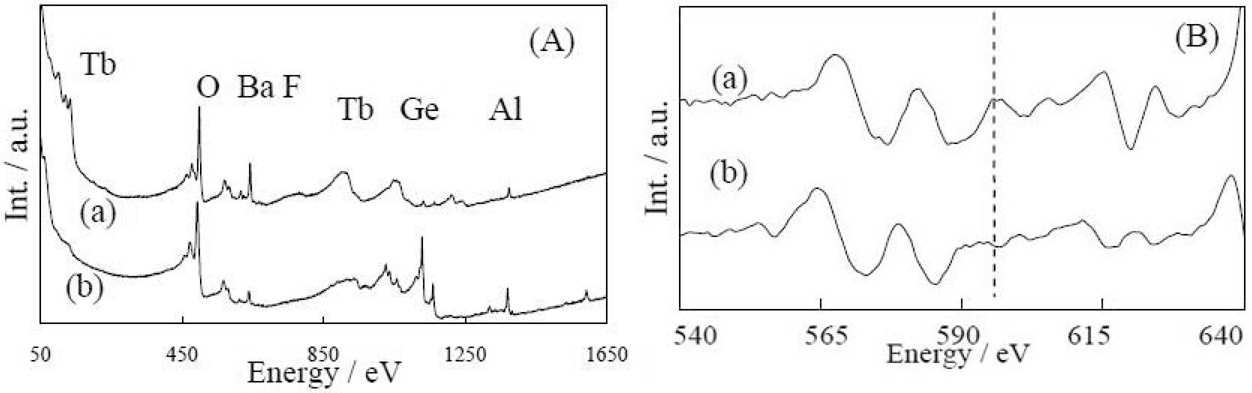

*Fig.1 AES spectra (wide (A) and narrow differential (B)) of oxide fluoride glasses. ((a) 40$TbF_3$ -20$BaF_2$ -10$AlF_3$ -30$GeO_2$ glass, (b) 10$TbF_3$ -20$BaF_2$ -10$AlF_3$ -60$GeO_2$ glass)*

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## P2.80

# Surface Fluorination of $LiNi_{0.5}Mn_{1.5}O_4$ Spinel as the Cathode Active Material for Li-ion Battery

**Y. SHIMIZU** [a]*, **J. KIM** [b], **J. IMAIZUMI** [b], **S. YONEZAWA** [a], **M. TAKASHIMA** [b]

[a] UNIVERSITY OF FUKUI, DEPT.MATERIALS SCI. & ENG. - FUKUI (JAPAN)
[b] UNIVERSITY OF FUKUI - FUKUI (JAPAN)

* yusuke_shimizu1031@yahoo.co.jp

$LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ have been used as the cathode active materials in the lithium ion batteries. Among these materials, $LiNi_{0.5}Mn_{1.5}O_4$ has the crystal structure in which a part of Mn in $LiMn_2O_4$ is replaced by Ni and shows high operation potential near 5V, so it is attracted as a high energy density cathode active material [1]. Until now, it has been found that surface modification of cathode active materials by fluorine gas must improve the thermal stability and the cycle ability of electrode[2]. In this study, surface fluorination of $LiNi_{0.5}Mn_{1.5}O_4$ was carried out and its electrochemical and thermal properties were examined in this study.

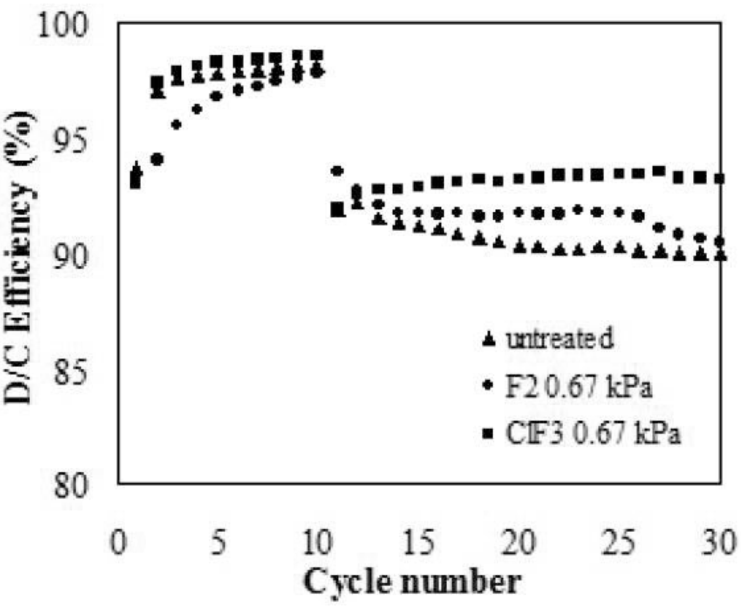

*Fig.1 Efficiency during charge/discharge cycle test of untreated and fluorinated samples.*

Surface fluorination of $LiNi_{0.5}Mn_{1.5}O_4$ with $F_2$ gas or $ClF_3$ gas was carried out at room temperature (RT) for 1h and treatment pressure of $F_2$ or $ClF_3$ was 0.67 kPa and 6.67 kPa. The cathode mixture consisted of the active material (untreated or fluorinated), acetylene black (AB) and polyvinylidene fluoride (PVDF) in the weight ratios of 8:1:1. And then NMP was added to the mixture and it was homogenized in a ball mill. After it was spread onto the aluminium foil and dried at 120 °C. Lithium metal foil was used as a counter electrode. 1.0mol/L $LiPF_6$ / EC+DMC (3:7vol) was used as an electrolyte solution. Electrochemical measurements were performed using Tom cell (like a coin cell). Charge and discharge test was carried out at room temperature during 10 cycles and 20 cycles were carried out at 60 °C after 10th cycle. From the result of XPS spectra (F 1s), it was thought that fluorine existed only on the surface because the peak of fluorine decreased by etching.

Fig.1 shows D/C efficiency (discharge/charge capacities) of the untreated and fluorinated samples. The efficiency of $LiNi_{0.5}Mn_{1.5}O_4$ fluorinated at 0.67 kPa (by $F_2$ and $ClF_3$) was improved compared to that of untreated one. The fluorine on the surface of $LiNi_{0.5}Mn_{1.5}O_4$ may stabilize a crystal structure near the surface and the side reaction was controlled.

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**P2.81**

# The structure and properties of the low-temperature fractions obtained by separation of ultrafine polytetrafluoroethylene (UPTFE-FORUM)

**L.N. IGNATEVA** [(a)*], **O.M. GORBENKO** [(a)], **N.N. SAVCHENKO** [(a)], **A.D. PAVLOV** [(a)], **V.M. BOUZNIK** [(b)]

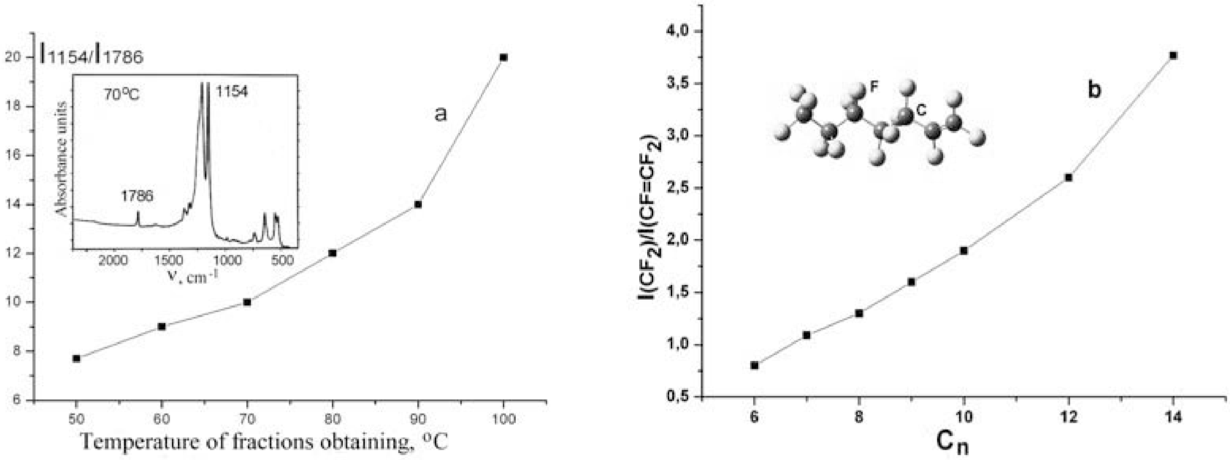
[(a)] INSTITUTE OF CHEMISTRY FEB RAS - VLADIVOSTOK (RUSSIA)

[(b)] A.A. BAIKOV INSTITUTE OF METALLURGY AND MATERIALS SCIENCE RAS - MOSCOW (RUSSIA)

* ignatieva@ich.dvo.ru

The low molecular fluoropolymers, that already have practical applications for coatings, nanofilms and nanocomposites, have attracted considerable interest among varying fluoropolymers. The powder ultrafine polytetrafluoroethylene (UPTFE-FORUM) is well known among of such materials [1]. The possibilities to separate powder into low-, medium-and high-molecular fraction, each of which has its own characteristics and different areas of practical application were revealed [2]. This served as a prerequisite for more fine separation of this material into fractions and their further study.

This paper presents a study of low molecular fractions of UPTFE-FORUM which were obtained by heating to 50-100°C with intervals separating 10 degrees. The experimental studies of the molecular composition and structure of the fractions, the phase structure, morphology and thermal properties were performed. Problem of unambiguous and reliable interpretation of empirical data from IR and NMR spectroscopy methods was solved by performing quantum chemistry calculations of the model polymer units. Calculated models were as close to the objects studied experimentally, $C_nF_{2n+2}$, $C_nF_{2n}$ (n=5-13). The calculations of energetic properties of constitutional isomers were performed. The formation of radicals and branches in fluorocarbon molecules, geometric parameters, preferred conformations, IR- and NMR-spectra of polymers and identification of polymer groups are discussed based on obtained results.



*The dependence of the peak intensities of the bands at 1154 cm $^{-1}$ and 1786 cm $^{-1}$ in the IR spectra of fractions: a - experimental values, b - calculated values.*

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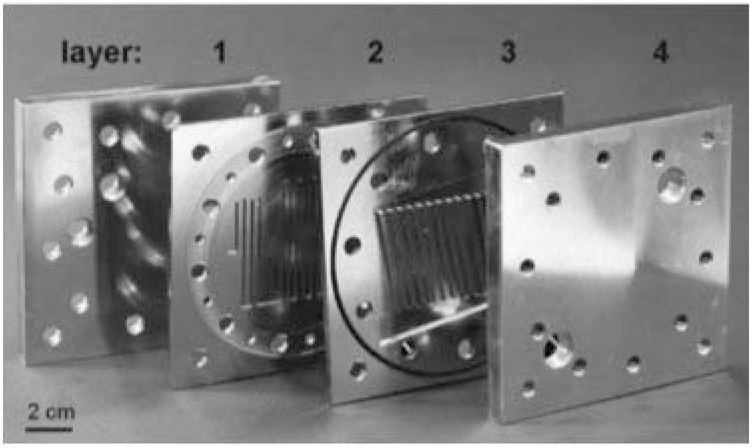
## P2.82

# Mini Reactor for the Direct Fluorination of Ethylencarbonate

**P. ZHANG [(a)], M. HILL [(a)], S. GOLL [(a)], P. LANG [(b)], P. WOIAS [(b)], I. KROSSING [(a)]***

[(a)] Institute for Inorganic and Analytical Chemistry, University of Freiburg - FREIBURG (GERMANY)
[(b)] Dept. for Microsystem Enginieering Freiburg (IMTEK), Universitäty of Freiburg - FREIBURG (GERMANY)

* ingo.krossing@ac.uni-freiburg.de



*Picture of the minireactor before being assembled. Layers: 1) inlets and outlets 2) reaction channels and channels for temperature sensors, 3) cooling channels, 4) inlets for cooling.*

The fluorination of organic and inorganic substances is frequently investigated in fundamental features and industrial applications. The problem of the direct fluorination is based on its very fast and exothermic reaction with carbohydrates. The potential hereby is the using of the concept of contacting gas and liquid media within a mini reactor. The main advantages of such reactors, like an excellent heat control, are connected to their very high surface to volume ratio due to the very small channel size. The direct fluorination of ethylene carbonate [1] was examined with using fluorine contents up to 88 % in nitrogen carrier gas. The decomposition stability of the carbon backbone in the direct fluorination is very high, which makes ethylene carbonate an interesting substrate for this reaction. Additionally fluorinated cyclic carbonates already have an industrial application, as solvents additives for lithium ion battery technologies.

Mini reactor [2]

The reactor was made of nickel coated copper blocks (Fig. 1). It is equipped with a meandered reaction channel, integrated temperature sensors and a potent active cooling system. The reaction channel diameter is 1 mm with a length of 35 cm after the gas inlet. This reactor is designed to get reasonable data for the further development of a microreactor which will be silicon chip based. The reactor was optimised for slug flow.

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## P2.83

# [$^{18}$F]-Fluorination of 4-[(halogeno or sulfonyloxy)methyl]piperidines: a comparative experimental and mechanistic study

**M. KEITA (a), S. SCHMITT (a), G. DUPAS (b), R. BROWN (c), C. PERRIO (d)***
(a) LDM-TEP, UMR6301 ISTCT, Cyceron, CNRS-CEA-UCBN - CAEN (FRANCE)
(b) UNIVERSITÉ DE ROUEN, UMR CNRS 6014 COBRA - MONT SAINT AIGNAN (FRANCE)
(c) School of Chemistry, University of Southampton - SOUTHAMPTON (UNITED KINGDOM)
(d) LDM-TEP, UMR6301 ISTCT, CNRS, CEA, Unicaen, UMR 6301 ISTCT - CAEN (FRANCE)
* perrio@cyceron.fr

Objectives. 4-(Fluoromethyl)piperidines are valuable molecular frameworks for drug discovery programs targeting central nervous system disorders and cancers. Therefore, the development of original 4-[$^{18}$F]-(fluoromethyl)piperidine containing radiopharmaceuticals is useful for PET imaging. In order to access to these structures, we examined the nucleophilic attack of [$^{18}$F]fluoride with a series of *N*-substituted 4-(halogeno- or sulfonyloxymethyl)piperidines 1. We postulated that such a reaction could occur either via a classical SN$_2$ reaction or via an intramolecular quaternarization of the piperidine nitrogen followed by a ring opening of the resulting bridged bicyclic quaternary ammonium salt to give the corresponding piperidine products 2 and/or the pyrrolidine derivatives 3 [1,2]. For a complete investigation, we studied both the radiofluorination and fluorination of piperidines 1. We also performed mechanistic studies including theoretical calculations at the B3LYP/6-311+G** level to characterize all the involved intermediates and transitions states and to calculate their activation energies.
Results. The fluorination and radiofluorination of *N*-Boc-piperidines 1a led exclusively to the corresponding fluoromethylpiperidines 2a in satisfactory yields (50-60%) and radiochemical yields (60-75%) under smooth conditions (90°C). From *N*-alkyl and *N*-arylpiperidines 1b, fluorinations failed whereas radiofluorinations were efficient (> 80%) when performed above 125°C. In the latter case, a mixture of 4-[$^{18}$F]-(fluoromethyl)piperidines 2b and 3-[$^{18}$F]-(fluoroethylpyrrolidines 3b was obtained in a ratio depending either on the *N*-alkyl/aryl substituent and the leaving group. Calculations of activation energies for the transition states corresponding to the formation of pyrrolidine and piperidine products were in accordance with the experimental results.
Conclusion. The radiofluorination of piperidines 1 was efficient and general. The selectivity of the radioactive reaction (formation of piperidines 2 vs pyrrolidines 3) was dependent on the starting piperidines 1. Calculations could predict the formation of the final radioactive products. Extension of this approach to access to radiopharmaceuticals is underway.

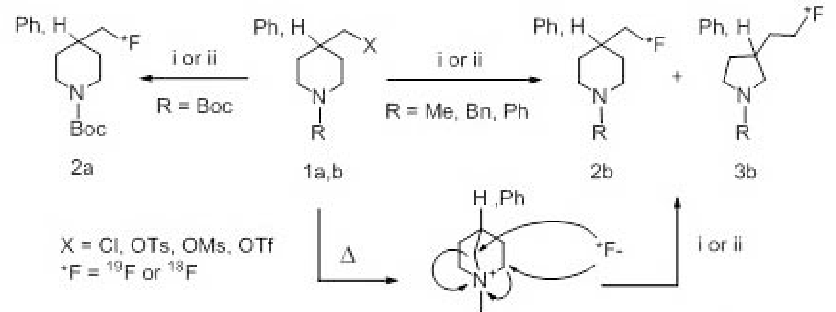

Fig.1. Fluorination and radiofluorination of piperidines **1**. (i) TBAF, KF or KF/K222, ACN or DMSO, 90-180°C, 2-24 h; (ii) K[$^{18}$F]F/K$_{222}$, ACN, DMF or DMSO, 50-180°C, 5-30 min.

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[1] C. Gilisen et al J Labelled Compd Radiopharm. **42** (1999), 1289.
[2] U. K. Bandarage et al Tetrahedron Lett. **51** (2010) 6415.

## P2.84

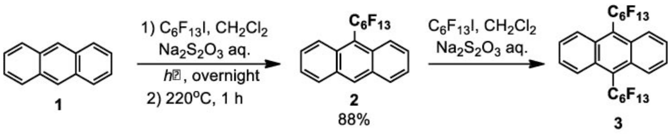
# Photoinduced Perfluoroalkylation of 9-Methylanthracene

**E. NOGAMI** [(a)]*, **T. YAJIMA** [(b)]

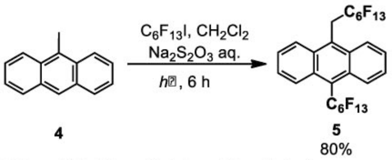
[(a)] OCHANOMIZU UNIVERSITY, YAJIMA LABORATORY - TOKYO (JAPAN)
[(b)] Ochanomizu University, CHEMISTRY - TOKYO (JAPAN)

* action.is.eloquence.23@gmail.com

Perfluoroalkylarenes and heteroarenes are becoming increasingly important compounds for pharmaceuticals, agrochemicals and functional materials. However, synthetic methods of the perfluoroalkylation of acenes have been limited. Thus, a mild and versatile method for the perfluoroalkylation of acenes is desirable. Under such circumstances, we have already developed the new photoinduced radical perfluoroalkylation of anthracene (Scheme 1) [1].



Scheme 1. Perfluoroalkylation of anthracene



Scheme 2. Perfluoroalkylation of 9-methylanthracene

During the study, we found that the radical perfluoroalkylation of 9-methylanthracene gave diperfluoroalkylated product 5, which is totally different from the product of the reaction of anthracene (Scheme 2). Here, we report the photoinduced perfluoroalkylation of 9-methylanthracene and structure analysis of the product.

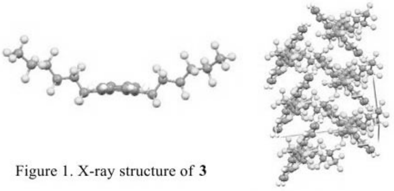


Figure 1. X-ray structure of **3**

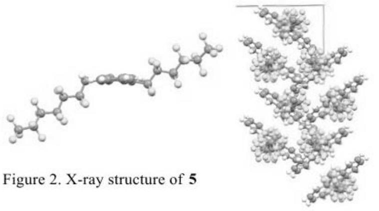


Figure 2. X-ray structure of **5**

First, the photoinduced reaction of perfluorohexyl iodide and 9-methylanthracene was examined. On the basis of the conditions used in our previous study, the reactions of 9-methylanthracene (1 equiv.) with perfluorohexyl iodide (2 equiv.) were carried out in the presence of aqueous $Na_2S_2O_3$ under UV irradiation in $CH_2Cl_2$. The reaction proceeded smoothly to give 9-perfluorohexyl-10-(perfluorohexylmethyl)anthracene 5 in good yield.

We then performed the X-ray single crystal structure analysis of product 3 and 5 to discuss the influence of perfluoroalkyl chains on the molecular alignment.

Compounds 3 and 5 are arranged in a herringbone motif without face-to-face π−π stacking in the crystal structure. The perfluoroalkyl chains of compound 3 were stretched out on the same side of the anthracene moiety. In contrast, those of compound 5 were on the different side.

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[1] E. Nogami, T. Yajima, T. Kubota, 20th International symposium on fluorine chemistry, P-76, 2012, Kyoto

## P2.85

# 3D Opal Nanosponge and Carbone-Fluorine Spectroscopy™: The Emergence of Nanotronics™ as Possible Nano-Fluoro-Theranostic Tool

**F. MENAA** [a]*, **B. MENAA** [b], **L. AVAKYANTZ** [c], **O. SHARTS** [c]

[a] Fluorotronics, Inc., Department of Pharmaceutical Sciences and Nanomedicine, FLUORINE CHEMISTRY AND NANOMEDICINE - CARLSBAD, CA (USA)
[b] Fluorotronics, Inc., Department of Chemical Sciences, Nanomaterials and Nanobiotechnology, Fluorotronics, Inc. - CARLSBAD, CA (USA)
[c] Fluorotronics, Inc., Department of Physical Sciences and Engineering, Department of Physical Sciences and Engineering - CARLSBAD, CA (USA)

* dr.fmenaa@gmail.com

Photonic crystals, or 3D photonic crystals, are monodispersed nanostructures than can have a regular lattice of structural elements of a size comparable with the wavelength of electromagnetic radiation in the visible range [1]. One example of a 3D photonic crystal is a $SiO_2$ amorphous material known as "synthetic opal," which is usually made of tightly and orderly packed $SiO_2$ spherical globules of equal size (Fig. 1). The spaces in synthetic opal can be filled with various compounds including fluoroorganics (e.g. F-drugs, F-biomolecules, F-polymers).

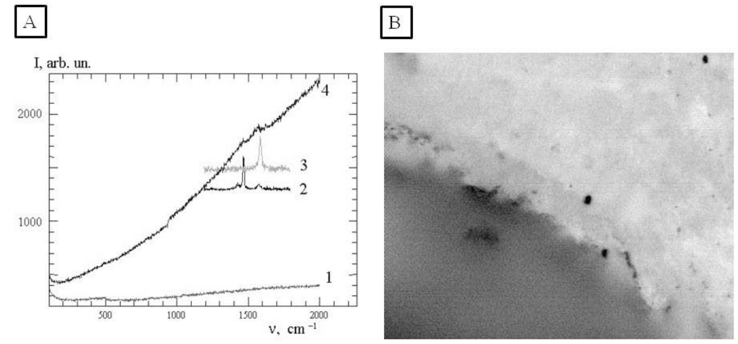

**Figure 4. Nanotronics™ spectra of nanoparticles and opal nanosponge™.**
Excitation was carried out by Ar-laser at 488 nm. On the *y*-axis, the legend "I, arb.un." refers to intensity, measured in arbitrary units. The *x*-axis represents the frequency, (wavelength number) measured in $cm^{-1}$. Enhanced intensity of 2 is observed when 2 (fullerene) is loaded in 1 (synthetic opal).
**A.** Spectrum of: **1**-Opal nanosponge™; **2**-pure fullerene; **3**-graphite; **4**-opal nanosponge™ filled with fullerene;
**B.** Morphological aspect of opal nanosponge.

We previously demonstrated that Carbon-Fluorine Spectroscopy (CFS™), *aka* Spectro-Fluor™ - a member tool from the PLIRFA™ (Pulsed Laser Isochronic Raman and Fluorine/Fluorescence Apparatus) platform - is a green, non-destructive, non-invasive, reliable and disruptive analytical technology that fits various pharmaceutical and bio-medical applications [1]. The key feature of CFS™ is based on the capability to specifically, sensitively and rapidly detect C-F bond(s) in the fingerprint spectral area of 550-850 cm-1 allowing F-imaging as well as qualitative and quantitative characterization of fluoroorganics *in vitro*, *ex-vivo* or *in-vivo* [2].

In the present work, we present a CFS™-derived application named Nanotronics™ (Fig. 2) which permits the characterization of fluoro-organics loaded into nanostructures (e.g. size determination of ultra-dispersed fluoro-polymers, length determination of fluorinated molecules entrapped into nanoparticles) (Fig. 3). Indeed, we show that the use of synthetic 3D-photonic opal $SiO_2$ nanosponge™ can enhance the unique Fluoro-Raman light scattering effects (about 104-106 folds), therefore allowing rapid, sensitive, specific detection and characterization of nanosponge-loaded fluoro-analytes (Fig. 4). Interestingly, preliminary data showed that Nanotronics™ could further synergize with other analytical tools (e.g. HTS, chromatography, microscopy, AFM) to implement the diagnosis and therapy (ex. screening, drug delivery, imaging, molecular interactions) [1,3].

Eventually, Nanotronics™ (a combination of CFS™ and opal nanosponges) is emerging as an innovative tool application to detect and characterize fluoroorganics loaded into nanostructures (e.g. 3D opal nanosponges) which could utilize theranostic approaches. We aim to present and discuss in more detail our advances in this area.

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[1] V. Gorelik, L. Zlobina, T. Murzina, *et al.* Spectra of 3D-photonic crystals coated by bismuth, K.C. *Physics*, N6 (2004), c.15.

[2] F. Menaa, B. Menaa, O. Sharts. Development of carbon-fluorine spectroscopy for pharmaceutical and biomedical applications. *Faraday Discuss.*, **149** (2011), 269-78; discussion 333-56.

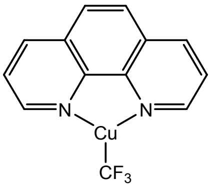
[3] O. Sharts, V. Gorelik et al. Opal Nanosponge as 3D Photonic Nanomaterial. *Pending patent*.

# INDEX

# Fluorination and Trifluoromethylation Selected Catalysts and Reagents

metals · inorganics · organometallics · catalysts · ligands · custom synthesis · cGMP facilities · nanomaterials

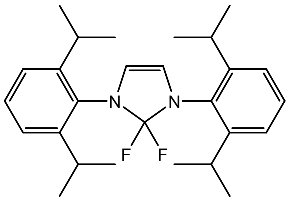
Reagent used for the perfluoromethylation of arenes and aryl bromides and iodides.

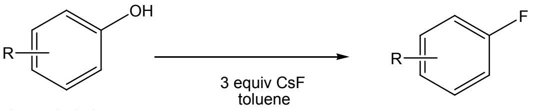


$$\text{Ar-I} \xrightarrow[\text{DMF, rt - 50}^{o}\text{C, 18 h}]{(\text{phen})\text{Cu-CF}_3} \text{Ar-CF}_3$$

**29-6720 Trifluoromethylator®**

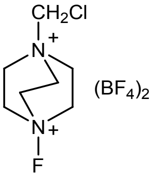
New, and operationally simple, deoxyfluorination reagent.





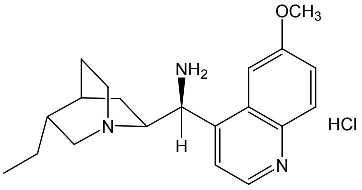
**07-0625 PhenoFluor™**

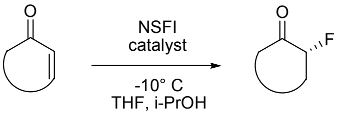
Reagent for electrophilic fluorination.



**07-0332 SelectFluor™**

α-fluorination of cyclic ketones.

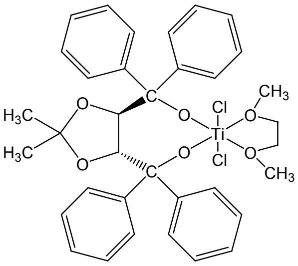


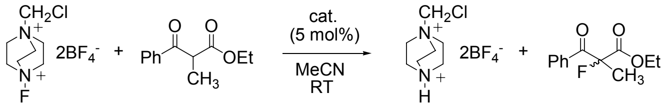


**07-1718 Cinchona alkaloid-derived Organocatalyst**

**See also 07-1710, 07-1715, 07-1722**

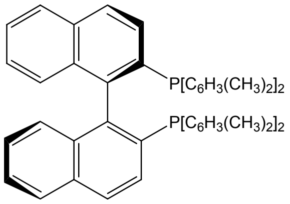
Catalyst used in the enantioselective fluorination of β-ketoesters.

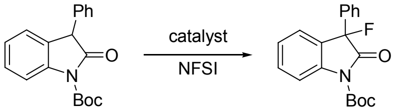




**22-0780 Togni Catalyst** **See also 22-0761**

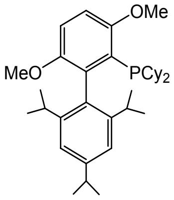
Ligand used in the enantioselective fluorination of oxindoles.

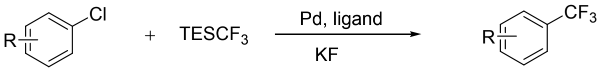




**15-0476 XylBINAP** **See also 15-0477, 15-0066, 15-0067**

Ligand for the palladium-catalyzed trifluoromethylation of aryl chlorides.





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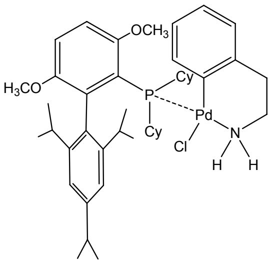

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**Strem Chemicals, Inc.**
7 Mulliken Way
Newburyport, MA 01950-4098
U.S.A.
Tel.: (978) 499-1600
Fax: (978) 465-3104
Email: info@strem.com

**Strem Chemicals, Inc.**
15, rue de l'Atome
Zone Industrielle
F-67800 BISCHHEIM France
Tel.: +33 (0) 3 88 62 52 60
Fax: +33 (0) 3 88 62 26 81
Email: info.europe@strem.com

**Strem Chemicals, Inc.**
Postfach 1215
D-77672 KEHL Germany
Tel.: +49 (0) 78 51 75879
Fax: +33 (0) 3 88 62 26 81
Email: info.europe@strem.com

**Strem Chemicals UK, Ltd.**
41 Hills Road
Cambridge
England CB2 1NT
Tel.: 0845 643 7263
Fax: 0845 643 7362
Email: enquiries@strem.co.uk

# PARTICIPANTS

**ADONIN Nicolay**
SB Russian Academy of Sciences, G.K. Boreskov Institute of catalysis
Novosibirsk *(Russia)*
adonin@catalysis.ru

**AHRENS Mike**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
mike.ahrens@staff.hu-berlin.de

**ALAZET Sebastien**
Université Claude Bernard – Lyon 1
Villeurbanne *(France)*
sebastien.alazet@gmail.com

**AL-MAHARIK Nawaf**
University of St Andrews
St Andrews *(UK)*
na10@st-andrews.ac.uk

**AMEDURI Bruno**
Institut Charles Gerhardt
Montpellier *(France)*
Bruno.ameduri@enscm.fr

**AMINE Khalil**
Argonne National Laboratory
Argonne, Il *(USA)*
amine@anl.gov

**ARKHIPENKO Sergey**
Moscow State University
Moscow *(Russia)*
fedorova@inorg.chem.msu.ru

**ASTRUC Arnaud**
Université de Poitiers – CNRS
Poitiers *(France)*
arnaud.astruc@univ-poitiers.fr

**AVAKYANTZ Lev**
Fluorotronics Inc.
Carlsbad, CA *(USA)*
leo.avakyantz@gmail.com

**AHRENS Theresia**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
ahrensth@cms.hu-berlin.de

**AKIYAMA Takahiko**
Gakushuin University
Tokyo *(Japan)*
takahiko.akiyama@gakushuin.ac.jp

**ALLEFELD Nadine**
Bielefeld University
Bielefeld *(Germany)*
nadine.allefeld@uni-bielefeld.de

**ALTY Adam**
Synquest Labs
Alachua *(USA)*
adam.alty@synquestlabs.com

**AMII Hideki**
Gunma University
Gunma *(Japan)*
amii@gunma-u.ac.jp

**ANTIPOV Evgeny**
Moscow State University
Moscow *(Russia)*
evgeny.antipov@gmail.com

**ASSUMMA Luca**
Université de Grenoble
Saint Martin d'Hères *(France)*
luca.assumma@libero.it

**AUBERT Corinne**
Université Pierre et Marie Curie
Paris *(France)*
corinne.aubert@upmc.fr

**BARDZINSKI Mateusz**
Adam Mickiewicz University
Poznan *(Poland)*
mateusz.bardzinski@gmail.com

**BAS Corine**
Université de Savoie
Le Bourget-du-Lac *(France)*
corine.bas@univ-savoie.fr

**BASA Anna**
University of Bialystok
Bialystok *(Poland)*
abasa@uwb.edu.pl

**BENZOUAA Rachid**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
rachid.benzouaa@univ-bpclermont.fr

**BERGER Josefine**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
bergerjo@student.hu-berlin.de

**BERLEMANN Hella**
Universität Münster
Münster *(Germany)*
berleman@uni-muenster.de

**BIGOT Bernard**
Commissariat à l'Energie Atomique, Fondation de la Maison de la Chimie
Paris *(France)*
presidence@maisondelachimie.com

**BILLARD Thierry**
Université Claude Bernard – Lyon 1
Villeurbanne *(France)*
thierry.billard@univ-lyon1.fr

**BINTEIN Fabrice**
Ministère de la Défense -DGA
Paris *(France)*
fabrice.bintein@intradef.gouv.fr

**BIRONNEAU Sonia**
INNOV'ORGA
Reims *(France)*
sonia.bironneau@innovorga.com

**BLIN Jean-Luc**
Université de Lorraine-CNRS
Vandoeuvre-Les-Nancy *(France)*
Jean-Luc.Blin@univ-lorraine.fr

**BOCA Miroslav**
FEB Russian Academy of Sciences
Bratislava *(Slovakia)*
miroslav.boca@savba.sk

**BOLTALINA Olga**
Colorado State University
Fort Collins, Co *(USA)*
olga.boltalina@colostate.edu

**BOMKAMP Martin**
Solvay Fluor GmbH
Hannover *(Germany)*
martin.Bomkamp@solvay.com

**BONNET Pierre**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
pierre.m.bonnet@univ-bpclermont.fr

**BONNET Philippe**
Arkema, CRRA
Pierre-Bénite *(France)*
philippe.bonnet@arkema.com

**BONNET-DELPON Daniele**
Université Paris Sud, Faculté de Pharmacie
Châtenay-Malabry *(France)*
daniele.bonnet-delpon@u-psud.fr

**BOUCHET Renaud**
Institut Polytechnique de Grenoble
Grenoble *(France)*
Renaud.Bouchet@lepmi.grenoble-inp.fr

**BOUGON Roland**
Champfol *(France)*
rol.bougon@orange.fr

**BOUILLON Jean-Philippe**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
jean-philippe.bouillon@univ-rouen.fr

**BOUR Daniel**
A3V-Studio
Penchard *(France)*
daniel.bourlevrai@free.fr

**BOURGEOIS Damien**
Commissariat à l'Energie Atomique, ICSM-LCPA
Bagnols-Sur-Cèze *(France)*
damien.bourgeois@cea.fr

**BRAUN Max**
Solvay Fluor GmbH
Hannover *(Germany)*
max.braun@solvay.com

**BRIGAUD Thierry**
Universite de Cergy-Pontoise
Cergy-Pontoise *(France)*
thierry.brigaud@u-cergy.fr

**BRUNET Sylvette**
Université de Poitiers-CNRS
Poitiers *(France)*
sylvette.brunet@univ-poitiers.fr

**BUCHWALD Stephen**
MIT
Cambridge, Ma *(USA)*
sbuchwal@mit.edu

**BUDNIKOVA Yulia**
A.E. Arbuzov Institute of Organic & Physical Chemistry
Kazan *(Russia)*
yulia@iopc.ru

**CAHARD Dominique**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
dominique.cahard@univ-rouen.fr

**CALLEJA Gérard**
SudFluor
Montpellier *(France)*
gerard.calleja@sudfluor.fr

**CAMPAGNE Benjamin**
Institut Charles Gerhardt
Montpellier *(France)*
benjamin.campagne@enscm.fr

**CASABURO Bruno**
Daikin Chemicals
Pierre Benite *(France)*
bcasaburo@daikinchemical.fr

**CELERIER Stephane**
Université de Poitiers - CNRS
Poitiers *(France)*
stephane.celerier@univ-poitiers.fr

**CHAKRABORTY Debi**
Sigma-Aldrich
Poole *(UK)*
debi.chakraborty@sial.com

**CHAMINADE Jean-Pierre**
ICMCB-CNRS
Pessac *(France)*
Chamin@imcb-bordeaux.cnrs.fr

**CHAMPAGNE Pier Alexandre**
Université Laval
Québec *(Canada)*
pier-alexandre.champagne.1@ulaval.ca

**CHATAIN Sylvie**
Commissariat à l'Energie Atomique,
DPC/SCCME/LM2T,
Gif-Sur-Yvette *(France)*
sylvie.chatain@cea.fr

**CHAUME Grégory**
Université de Cergy-Pontoise
Cergy-Pontoise *(France)*
gregory.chaume@u-cergy.fr

**CHAUVEAU Jérome**
Arkema Cerdato
Serquigny *(France)*
jerome.chauveau@arkema.com

**CHERNYKH Yana**
IOCB - ASCR
Prague *(Czech Republic)*
per4eny@gmail.com

**CHO Seho**
Chungnam National University
Daejeon *(Korea)*
sehcho@cnu.ac.kr

**CHRISTE Karl**
University of Southern California
Los Angeles, Ca *(USA)*
kchriste@usc.edu

**COLOMB Julie**
Université Claude Bernard – Lyon 1
Villeurbanne *(France)*
julie.colomb@live.fr

**COMPAIN Guillaume**
University of Southampton
Southampton *(UK)*
g.compain.gc@gmail.com

**CORR Michael**
University of St Andrews
St Andrews *(UK)*
mc410@st-andrews.ac.uk

**COUTURE Guillaume**
Institut Charles Gerhardt
Montpellier *(France)*
guillaume.couture@enscm.fr

**CRASSOUS Isabelle**
Areva NC
Pierrelatte *(France)*
Isabelle.crassous@areva.com

**CROUSE Philip**
University of Pretoria
Pretoria *(South Africa)*
philip.crouse@up.ac.za

**CROUSSE Benoit**
Université Paris Sud, Faculté de Pharmacie
Châtenay-Malabry *(France)*
benoit.crousse@u-psud.fr

**CYTLAK Tomasz**
Adam Mickiewicz University
Poznan *(Poland)*
cytlak@amu.edu.pl

**DAI Xiaoyang**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
xiaoyang.dai@insa-rouen.fr

**DAMBOURNET Damien**
PECSA, Université Pierre et Marie Curie,
Paris *(France)*
damien.dambournet@upmc.fr

**DAMS Rudy**
3M Belgium
Zwijndrecht *(Belgium)*
rdams1@mmm.com

**DANKOV Yury**
JSC Perm Chemical Company
Perm *(Russia)*
dankov@inbox.ru

**DECAMPS Sophie**
BIOCIS, Université Paris-Sud
Châtenay-Malabry *(France)*
sophie.decamps@u-psud.fr

**DEL GUERZO André**
Université Bordeaux 1
Talence *(France)*
andre.del-guerzo@u-bordeaux1.fr

**DEL POZO Carlos**
University of Valencia
Burjassot *(Spain)*
carlos.pozo@uv.es

**DELPECH Sylvie**
CNRS - IPN
Orsay *(France)*
delpech@ipno.in2p3.fr

**DEMOURGUES Alain**
ICMCB-CNRS
Pessac *(France)*
demourg@icmcb-bordeaux.cnrs.fr

**DESMARTEAU Darryl**
Clemson University
Anderson, Sc *(USA)*
FLUORIN@CLEMSON.EDU

**DEVILLERS Emmanuelle**
Université de Cergy-Pontoise
Cergy-Pontoise *(France)*
emmanuelledevillers@yahoo.fr

**DEVILLERS Didier**
PECSA, Université Pierre et Marie Curie
Paris *(France)*
didier.devillers@upmc.fr

**DITER Patrick**
Université de Versailles-Saint Quentin-CNRS
Versailles *(France)*
patrick.diter@uvsq.fr

**DOLOVANYUK Violetta**
NUAS, Institute of Bioorganic Chemistry &
Petrochemistry
Kyiv *(Ukraine)*
flower_violet@ukr.net

**DU Ruobing**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
duruobing@sioc.ac.cn

**DUBOIS Marc**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
marc.dubois@univ-bcplermont.fr

**DUDA Blazej**
FU Berlin
Berlin *(Germany)*
blazejduda@gmail.com

**DUGERT Henri**
Maison de la Chimie
Paris *(France)*
h.dugert@maisondelachimie.com

**DUL Marie-Claire**
Commissariat à l'Energie Atomique, ICSM
Bagnols-Sur-Cèze *(France)*
marie-claire.dul@cea.fr

**DURAND Etienne**
ICMCB-CNRS
Pessac *(France)*
edurand@icmcb-bordeaux.cnrs.fr

**DUTTINE Mathieu**
PECSA, Université Pierre et Marie Curie-CNRS
Paris *(France)*
mathieu.duttine@upmc.fr

**DYACHENKO Alexander**
Tomsk Polytechnic University
Tomsk *(Russia)*
atom@tpu.ru

**EAST Michael**
Tosoh USA
Golf, Illinois *(USA)*
michael.east@tosoh.com

**ELLWANGER Matias**
Albert-Ludwigs Universität Freiburg
Kirchzarten *(Germany)*
mathias.ellwanger@gmx.net

**FEDOROV Pavel**
Russian Academy of Sciences, A.M. Prokhorov
General Physics Institute
Moscow *(Russia)*
ppfedorov@yandex.ru

**FEDOROVA Anna**
Moscow State University
Moscow *(Russia)*
annaaf@mail.ru

**FELLER Michael**
Ludwig-Maximilian University,
Munich *(Germany)*
michael.feller@cup.uni-muenchen.de

**FEREY Gérard**
Member of the French Academy of Science,
President of IAB
Paris *(France)*
gferey@gmail.com

**FICHTNER Maximilian**
Karlsruhe Institute of Technology
Ulm *(Germany)*
m.fichtner@kit.edu

**FILATOV Andrey**
National Academy of Sciences of Ukraine
Kyiv *(Ukraine)*
filatov@ioch.kiev.ua

**FILINCHUK Yaroslav**
Université Catholique de Louvain
Louvain-La-Neuve *Belgium*
yaroslav.filinchuk@uclouvain.be

**FLAHAUT Delphine**
Université de Pau
Pau *(France)*
delphine.flahaut@univ-pau.fr

**FLECHE Jean-Louis**
Commissariat à l'Energie Atomique
Gif-Sur-Yvette *(France)*
jean-louis.fleche@cea.fr

**FLEROV Igor**
Kirensky Institute of Physics
Krasnoyarsk *(Russia)*
flerov@iph.krasn.ru

**FRANK Walter**
Heinrich-Heine-Universität
Düsseldorf *(Germany)*
wfrank@uni-duesseldorf.de

**FRIESEN Chadron M.**
Trinity Western University
Langley, Bc *(Canada)*
chad.friesen@twu.ca

**FRUEH Natalja**
ETH Zürich
Zürich *(Switzerland)*
frueh@inorg.chem.ethz.ch

**FUKUMOTO Hiroki**
Ibaraki University
Hitachi *(Japan)*
hfukumot@mx.ibaraki.ac.jp

**GALIMBERTI Marco**
Solvay Specialty Polymers
Bollate, Milano *(Italy)*
marco.galimberti@solvay.com

**GATENYO Julia**
Tel Aviv University
Tel Aviv *(Israel)*
julialur@post.tau.ac.il

**GERKEN Michael**
University of Lethbridge
Lethbridge, Alberta *(Canada)*
michael.gerken@uleth.ca

**GERUS Igor**
NAS, Institute of Bioorganic Chemistry &
Petrochemistry
Kyiv *(Ukraine)*
igerus@hotmail.com

**GLADOW Daniel**
FU Berlin
Berlin *(Germany)*
Daniel.Gladow@Chemie.FU-Berlin.de

**GOETTEL James**
University of Lethbridge
Lethbridge, Alberta *(Canada)*
jamiegoettel@gmail.com

**GOLA Massimo**
Politecnico di Milano
Milano *(Italy)*
massimo.gola@chem.polimi.it

**GORBAN Oksana**
Nas of Ukraine, Donetsk Institute For Physics & Engineering
Donetsk *(Ukraine)*
oxanag1@ukr.net

**GOTO Takuya**
Doshisha University
Kyotanabe, Kyoto *(Japan)*
tgoto@mail.doshisha.ac.jp

**GOUMAIN Sophie**
INNOV'ORGA
Reims *(France)*
sophie.goumain@innovorga.com

**GOUVERNEUR Veronique**
Oxford University
Oxford *(UK)*
veronique.gouverneur@chem.ox.ac.uk

**GRAS Emmanuel**
CNRS - Université Paul Sabatier
Toulouse *(France)*
emmanuel.gras@lcc-toulouse.fr

**GREDIN Patrick**
LMCP, Université Pierre et Marie Curie
Paris *(France)*
patrick.gredin@upmc.fr

**GRELLEPOIS Fabienne**
Université de Reims-Champagne-Ardenne
Reims *(France)*
fabienne.grellepois@univ-reims.fr

**GRENIER Antonin**
PECSA, Université Pierre et Marie Curie
Paris *(France)*
antonin.grenier@upmc.fr

**GROCHALA Wojciech**
Warsaw University,
Warsaw *(Poland)*
wgroch@chem.uw.edu.pl

**GROMOV Oleg**
JSC «Leading Scientific Research Institute of Chemical Technology»
Moscow *(Russia)*
ollgromov@mail.ru

**GROULT Henri**
PECSA, Université Pierre et Marie Curie
Paris *(France)*
henri.groult@upmc.fr

**GUERIN Katia**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
katia.guerin@univ-bpclermont.fr

**GUEYRARD David**
Université Claude Bernard – Lyon 1
Villeurbanne *(France)*
david.gueyrard@univ-lyon1.fr

**GUITTARD Frederic**
University of Nice Sophia Antipolis
Nice *(France)*
Frederic.GUITTARD@unice.fr

**GUO Yong**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
yguo@sioc.ac.cn

**HAGIWARA Rika**
Kyoto University
Kyoto *(Japan)*
hagiwara@energy.kyoto-u.ac.jp

**HAMILTON Neil**
Apollo Scientific Ltd
Stockport *(UK)*
Neil.Hamilton@apolloscientific.co.uk

**HAMWI André**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
Andre.HAMWI@univ-bpclermont.fr

**HANAMOTO Takeshi**
Saga University
Saga *(Japan)*
hanamoto@cc.saga-u.ac.jp

**HANER Jamie**
McMaster University
Hamilton, On *(Canada)*
hanerj@mcmaster.ca

**HEINRICH Darina**
FU Berlin
Berlin *(Germany)*
dheinrich@zedat.fu-berlin.de

**HIRANO Kazuhiro**
Permelec Electrode Ltd.
Fujisawa *(Japan)*
hirano@permelec.co.jp

**HODGSON Emma**
Mexichem Fluor UK
Runcorn *(UK)*
emma.hodgson@mexichem.com

**HOLZE Patrick**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
patrick.holze@chemie.hu-berlin.de

**HORCAJADA Patricia**
Université de Versailles-Saint Quentin-CNRS
Versailles *(France)*
patricia.horcajada@uvsq.fr

**HORI Akiko**
Kitasato University
Sagamihara-Shi, Kanagawa *(Japan)*
hori@kitasato-u.ac.jp

**HUHMANN Susanne**
FU Berlin
Berlin *(Germany)*
susanne.huhmann@fu-berlin.de

**IANNARELLI Chantal**
Congrès Scientifiques Services
Saint Cloud *(France)*
c2smail@yahoo.fr

**IGNATIEVA Lidiia**
FEB Russian Academy of Sciences
Vladivostok *(Russia)*
ignatieva@ich.dvo.ru

**HAUFE Günter**
Universität Münster
Münster *(Germany)*
haufe@uni-muenster.de

**HIRAMATSU Shinji**
Okoyama University
Okayama *(Japan)*
en20246@s.okayama-u.ac.jp

**HIROTAKI Kensuke**
Saga University
Saga *(Japan)*
11634014@edu.cc.saga-u.ac.jp

**HOGE Berthold**
Bielefeld University
Bielefeld *(Germany)*
b.hoge@uni-bielefeld.de

**HOPPMANN Simone**
ABCR GmbH & Co. KG
Karlsruhe *(Germany)*
s.hoppmann@abcr.de

**HORI Hisao**
Kanagawa University
Hiratsuka *(Japan)*
h-hori@kanagawa-u.ac.jp

**HOSEK Jan**
Institute of Chemical Technology
Prague *(Czech Republic)*
hosekj@vscht.cz

**HUNTER Luke**
The University of New South Wales
Sydney, NSW *(Australia)*
l.hunter@unsw.edu.au

**IGNATIEV Nikolai**
Merck KGaA
Darmstadt *(Germany)*
nikolai.ignatiev@merck.de

**IKEDA Akari**
Setsunan University
Hirakata *(Japan)*
12d401ia@edu.setsunan.ac.jp

**IRITA Tomomi**
Daikin Industries Ltd.
Settsu-Shi-Osaka *(Japan)*
tomomi.irita@daikin.co.jp

**ISODA Motoyuki**
Setsunan University
Hirakata-Osaka *(Japan)*
12d402im@edu.setsunan.ac.jp

**ITOH Toshiyuki**
Tottori University
Tottori City *(Japan)*
titoh@chem.tottori-u.ac.jp

**IVASHKIN Pavel**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
pavelivashkin@gmail.com

**IVLEV Sergey**
Tomsk Polytechnic University
Tomsk *(Russia)*
ivlev@tpu.ru

**JAGLICIC Zvonko**
University of Ljubljana
Ljubljana *(Slovenia)*
zvonko.jaglicic@imfm.si

**JAUNZEMS Janis**
Solvay Fluor GmbH
Hannover *(Germany)*
janis.jaunzems@solvay.com

**JEONG In Howa**
Yonsei University
Wonju, Gangwondo *(S. Korea)*
jeongih@yonsei.ac.kr

**JUBAULT Philippe**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
philippe.jubault@insa-rouen.fr

**JUREK Joanna**
Adam Mickiewicz University
Poznan *(Poland)*
joannajurek1989@gmail.com

**KALINOVICH Nataliya**
Jacobs University
Bremen *(Germany)*
n.kalinovich@jacobs-university.de

**KANAKI Elisavet**
Institute für chemie and biochemie
Berlin *(Germany)*
kanaki@chemie.fu-berlin.de

**KANEGA Jun**
Unimatec Chemicals Europe GMbH & Co. KG
Weinheim *(Germany)*
jun.kanega@unimatec-europe.com

**KASUBKE Michael**
Solvay Fluor GmbH
Hannover *(Germany)*
michael.kasubke@solvay.com

**KATAGIRI Toshimasa**
Okoyama University
Okayama *(Japan)*
tkata@cc.okayama-u.ac.jp

**KAVUN Valeriy**
FEB Russian Academy of Sciences
Vladivostok *(Russia)*
kavun@ich.dvo.ru

**KAWADA Kosuke**
Tosoh F-Tech. Inc
Shunan Yamaguchi *(Japan)*
kosuke-kawada@f-techinc.co.jp

**KAZMIERCZAK Marcin**
Adam Mickiewicz University
Poznan *(Poland)*
marcin.kazmierczak@amu.edu.pl

**KEDDIE Neil**
University of St Andrews
St Andrews, Fife *(UK)*
nsk@st-andrews.ac.uk

**KHARCHENKO Valeriy**
Institute of Chemistry, ESQCS
Vladivostok *(Russia)*
vikharchenko@gmail.com

**KIRSCH Peer**
Merck KGaA
Darmstadt *(Germany)*
peer.kirsch@merckgroup.com

**KOEHN Christiane**
Novaled AG
Dresden *(Germany)*
marlis.daebritz@novaled.com

**KONINGS Rudy**
European Commission, Institute For Transuranium Elements
Karlsruhe *(Germany)*
rudy.konings@ec.europa.eu

**KORONIAK Henryk**
Adam Mickiewicz University
Poznan *(Poland)*
koroniak@amu.edu.pl

**KRAYDENKO Roman**
Tomsk Polytechnic University
Tomsk *(Russia)*
kraydenko@tpu.ru

**KUBIKOVA Blanka**
Institute of Chemistry, Dept of Molten Salts
Bratislava *(Slovakia)*
blanka.kubikova@savba.sk

**KUKHAR Valery**
Institute of Bioorganic Chemistry & Petrochemistry,
Kyiv *(Ukraine)*
kukhar@bpci.kiev.ua

**KUZNETSOV Sergey**
A.M. Prokhorov General Physics Institute
Moscow *(Russia)*
kouznetzovsv@gmail.com

**KVICALA Jaroslav**
Institute of Chemical Technology
Prague *(Czech Republic)*
jaroslav.kvicala@vscht.cz

**LADMIRAL Vincent**
Institut Charles Gerhardt
Montpellier *(France)*
vincent.ladmiral@enscm.fr

**KLÖSENER Johannes**
Bielefeld University
Bielefeld *(Germany)*
johannes.kloesener@uni-bielefeld.de

**KONDRATOV Ivan**
ENAMINE Ltd
Kyiv *(Ukraine)*
Vanya_ko@mail.ru

**KORNATH Andreas**
Ludwig-Maximilian University
Munich *(Germany)*
andreas.kornath@cup.uni-muenchen.de

**KRAFFT Marie Pierre**
Université de Strasbourg - CNRS
Strasbourg *(France)*
krafft@unistra.fr

**KRüGER Juliane**
FU Berlin
Berlin *(Germany)*
juliane.krueger@fu-berlin.de

**KUBYSHKIN Vladimir**
Karlsruhe Institute of Technology
Karlsruhe *(Germany)*
vladimir.kubyshkin@kit.edu

**KüTT Agnes**
University of Tartu
Tartu *(Estonia)*
agnes.kutt@ut.ee

**KUZNETSOV Sergey**
Kola Science Centre
Apatity *(Russia)*
kuznet@chemy.kolasc.net.ru

**LACROIX Marc**
Solvay Fluor GmbH
Hannover *(Germany)*
marc.lacroix@solvay.com

**LAMANDE-LANGLE Sandrine**
Université de Lorraine-CNRS
Vandoeuvre-Les-Nancy *(France)*
sandrine.langle@srsmc.uhp-nancy.fr

**LANDELLE Grégory**
Université de Strasbourg
Strasbourg *(France)*
gregory.landelle@gmail.com

**LAPTASH Nataly**
Institute of Chemistry
Vladivostok *(Russia)*
laptash@ich.dvo.ru

**LE DARZ Alexandre**
Sarl @rtMolecule
Poitiers *(France)*
alexandre.le.darz@univ-poitiers.fr

**LEE Young-seak**
Chungnam National University
Daejeon *(Republic of Korea)*
youngslee@cnu.ac.kr

**LEGEIN Christophe**
IMMM, Université du Maine
Le Mans *(France)*
Christophe.Legein@univ-lemans.fr

**LENSEN Nathalie**
Université de Cergy-Pontoise
Cergy Pontoise *(France)*
nathalie.lensen@u-cergy.fr

**LEQUEUX Thierry**
Université de Caen
Caen *(France)*
thierry.lequeux@ensicaen.fr

**LI Wei**
PECSA, Université Pierre et Marie Curie
Paris *(France)*
wei.li@upmc.fr

**LIGHTFOOT Philip**
University of St Andrews
St Andrews *(UK)*
pl@st-and.ac.uk

**LOPEZ Gerald**
Institut Charles Gerhardt
Montpellier *(France)*
Gerald.Lopez@enscm.fr

**LANGLOIS Bernard**
Université Claude Bernard – Lyon 1
Lyon *(France)*
bernard.langlois@univ-lyon1.fr

**LARNAUD Florent**
ENSICAEN, LCMT
Caen *(France)*
florent.larnaud@ensicaen.Fr

**LEBLANC Marc**
IMMM, Université du Maine
Le Mans *(France)*
marc.leblanc@univ-lemans.fr

**LEFCOSKI Stephan**
University of North Carolina
Charlotte *(USA)*
snlefcos@uncc.edu

**LEITZ Dominik**
LMU Munich
Munich *(Germany)*
dominikleitz@web.de

**LENTZ Dieter**
FU Berlin
Berlin *(Germany)*
lentz@chemie.fu-berlin.de/lentz@fu-berlin.de

**LEROUX Frédéric**
CNRS-Université de Strasbourg
Strasbourg *(France)*
frederic.leroux@unistra.fr

**LICHTENTHALER Martin R.**
University of Freiburg
Freiburg *(Germany)*
martin.lichtenthaler@ac.uni-freiburg.de

**LIN Jinhong**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
jlin@sioc.ac.cn

**LOUBAT Cédric**
Specific Polymers
Castries *(France)*
*cedric.loubat@specificpolymers.fr*

**LU Long**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
lulong@sioc.ac.cn

**LüDTKE Carsten**
FU Berlin
Berlin *(Germany)*
carstenl1986@zedat.fu-berlin.de

**LUI Norbert**
Bayer CropScience AG
Monheim *(Germany)*
norbert@lui@bayer.com

**LUXEN André**
Université de Liège PET Center
Liège *(Belgium)*
aluxen@ulg.ac.be

**MA Wei**
Kyushu University
Fukuoka *(Japan)*
m-wei@cstf.kyushu-u.ac.jp

**MABUDAFHASI Mbangiseni**
University of Pretoria
Pretoria *(South Africa)*
mbangiseni.mabudafhasi@necsa.co.za

**MACCONE Patrizia**
Solvay Specialty Polymers
Bollate, Milano *(Italy)*
patrizia.maccone@solvay.com

**MAGNIER Emmanuel**
Université de Versailles-Saint Quentin-CNRS
Versailles *(France)*
emmanuel.magnier@uvsq.fr

**MAISONNEUVE Vincent**
IMMM, Université du Maine
Le Mans *(France)*
vincent.maisonneuve@univ-lemans.fr

**MAJIMEL Jerome**
ICMCB-CNRS
Pessac *(France)*
majimel@icmcb-bordeaux.cnrs.fr

**MAKARENKO Natalia**
Chemistry Lab Rare Metals
Vladivostok *(Russia)*
makarenko@ich.dvo.ru

**MAKAROWICZ Anna-Maria**
ABCR GmbH & Co. KG
Karlsruhe *(Germany)*
a.makarowicz@abcr.de

**MAMONE Marius**
BIOCIS, Université Paris-Sud
Châtenay-Malabry *(France)*
marius.mamone@u-psud.fr

**MARCHIONNI Giuseppe**
Solvay Specialty Polymers
Bollate, Milano *(Italy)*
Giuseppe.marchionni@solvay.com

**MARCINIAK Bartosz**
Adam Mickiewicz University
Poznan *(Poland)*
barmar@amu.edu.pl

**MASCHKE Marcus**
Ruhr-Universität Bochum
Bochum *(Germany)*
marcus.maschke@rub.de

**MASHIMBYE Malhori**
Division Science & Technology
Pretoria *(South Africa)*
malhorimj@gmail.com
Mahlori.Mashimbye@dst.gov.za

**MATSNEV Andrii**
Clemson University
Anderson, Sc *(USA)*
a.v.matsnev@gmail.com

**MATSUMOTO Kazuhiko**
Kyoto University
Kyoto *(Japan)*
k-matsumoto@energy.kyoto-u.ac.jp

**MATTHEE Thorsten**
Condias GmbH
Itzehoe *(Germany)*
matthee@condias.de

**MAZEJ Zoran**
Jozef Stefan Institute
Ljubljana *(Slovenia)*
zoran.mazej@ijs.si

**MEAZZA Giovanni**
Isagro SpA
Novara *(Italy)*
gmeazza@isagro.it

**MEDEBIELLE Maurice**
Université Claude Bernard – Lyon 1
Lyon *(France)*
maurice.medebielle@univ-lyon1.fr

**MERCIER Anne-marie**
IMMM, Université du Maine
Le Mans *(France)*
anne-marie.mercier@univ-lemans.fr

**MESHRI Dayal T.**
Advance Research Chemicals Inc.
Catoosa, Ok *(USA)*
dr.meshri@fluoridearc.com

**METAYER Benoît**
Université de Poitiers – CNRS
Poitiers *(France)*
benoit.metayer@univ-poitiers.fr

**METRANGOLO Pierangelo**
Politecnico di Milano,
Milano *(Italy)*
pierangelo.metrangolo@polimi.it

**METZ François**
Solvay Recherches CRTL
St Fons *(France)*
francois.metz@solvay.com

**MEWS Rüdiger**
University of Bremen,
Bremen *(Germany)*
mewshome@uni-bremen.de

**MEYER Daniel**
Commissariat à l'Energie Atomique, ICSM
Bagnols-Sur-Cèze *(France)*
daniel.meyer@cea.fr

**MIKHAILICHENKO Sergey**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
misergey@yahoo.com

**MILCENT Thierry**
BIOCIS, Université Paris-Sud
Châtenay-Malabry *(France)*
thierry.milcent@u-psud.fr

**MITKIN Valentin**
Nikolaev Institute of Inorganic Chemistry
Novosibirsk *(Russia)*
mit48@mail.ru

**MIZUTA Shunpei**
Central Glass Europe Ltd.
Stockport *(UK)*
*shunpei.mizuta@cgco.co.jp*

**MOROZOV Igor**
Moscow State University
Moscow *(Russia)*
miv448@mail.ru

**MORTIER Michel**
ENSCP-Chimie ParisTech
Paris *(France)*
michel-mortier@chimie-paristech.fr

**MUNEMORI Daisuke**
Tottori University
Tottori City *(Japan)*
M12T4025M@edu.tottori-u.ac.jp

**MURPHY Cormac**
University College Dublin
Dublin *(Ireland)*
cormac.d.murphy@ucd.ie

**MYKHAILIUK Pavel**
ENAMINE Ltd
Kyiv *(Ukraine)*
Pavel.Mykhailiuk@mail.enamine.net

**NAKAJIMA Tsuyoshi**
Aichi Institute of Technology
Toyota *(Japan)*
nakajima-san@aitech.ac.jp

**NAPPA Mario**
E. I. Dupont de Nemours & Co.
Wilmington, De *(USA)*
mario.j.nappa@usa.dupont.com

**NI Chuanfa**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
nichuanfa@sioc.ac.cn

**NISHIMURA Fumihiro**
University of Fukui
Fukui *(Japan)*
fumihiro1986@gmail.com

**NOGAMI Emiko**
Ochanomizu University
Tokyo *(Japan)*
action.is.eloquence.23@gmail.com

**NYAKATURA Elisabeth**
FU Berlin
Berlin *(Germany)*
elisabeth.nyakatura@fu-berlin.de

**O'HAGAN David**
University of St Andrews
St Andrews *(UK)*
do1@st-andrews.ac.uk

**OMOTE Masaaki**
Setsunan University
Hirakata, Osaka *(Japan)*
omote@pharm.setsunan.ac.jp

**ONGERI Sandrine**
Université Paris-Sud
Châtenay-Malabry *(France)*
sandrine.ongeri@u-psud.fr

**OPEKAR Stanislav**
IOCB, ASCR
Praha *(Czech Republic)*
stanislav.opekar@post.cz

**ORTEL Marlis**
Jacobs University
Bremen *(Germany)*
m.ortel@jacobs-university.de

**OSTVALD Roman**
Tomsk Polytechnic University
Tomsk *(Russia)*
ostvald@tpu.ru

**OTTH Elisabeth**
ETH Zürich
Zürich *(Switzerland)*
elisabeth.otth@inorg.chem.ethz.ch

**PABON Martial**
DuPont de Nemours International
Geneva *(Switzerland)*
martial.pabon@dupont.com

**PAJKERT Romana**
Jacobs University
Bremen *(Germany)*
r.pajkert@jacobs-university.de

**PARIZEK Sven**
Heinrich-Heine-Universität
Düsseldorf *(Germany)*
sven.parizek@uni-duesseldorf.de

**PATARD Louis**
Histoire des Sciences
Paris *(France)*
louis_patard@yahoo.fr

**PAZENOK Sergii**
Bayer CropScience
Monheim *(Germany)*
sergiy.pazenok@bayer.com

**PEAN Clarisse**
PECSA, Université Pierre et Marie Curie
Paris *(France)*
clarisse.pean@upmc.fr

**PEDERSEN Kasper**
University of Copenhagen
Copenhagen *(Denmark)*
kaspersteenpedersen@gmail.com

**PEGOT Bruce**
Université de Versailles-Saint Quentin-CNRS
Versailles *(France)*
bruce.pegot@uvsq.fr

**PEPIN Cinta**
ICMCB-CNRS
Pessac *(France)*
pepin@icmcb-bordeaux.cnrs.fr

**PERNICE Holger**
Solvay Fluor GmbH
Hannover *(Germany)*
holger.pernice@solvay.com

**PERRIO Cécile**
CNRS-CEA-Unicaen
Caen *(France)*
perrio@cyceron.fr

**PERSICO Federico**
Politecnico di Milano
Milano *(Italy)*
fpersico@chem.polimi.it

**PETRIK Vitaliy**
Chemtaurus GmbH
Bremen *(Germany)*
vitpetrik@yahoo.com

**PEYROUX Jérémy**
Institut de Chimie de Clermont-Ferrand
Aubière *(France)*
jeremy.peyroux@univ-bpclermont.fr

**PICOT Stéphane**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
stephane.picot@univ-lyon1.fr

**POEPPELMEIER Kenneth**
Northwestern University
Evanston, Il *(USA)*
krp@northwestern.edu

**POLYSHCHUK Svetlana**
Institute of Chemistry
Vladivostok *(Russia)*
ignatieva@ich.dvo.ru

**POMINOVA Daria**
A.E. Arbuzov Institute of Organic & Physical Chemistry
Moscow *(Russia)*
pominovadv@rambler.ru

**PONOMARENKO Maxim**
Jacobs University
Bremen *(Germany)*
maxponom@yahoo.co.uk

**PORTAIL Nicolas**
Bio-logic SAS
Claix *(France)*
nicolas.portail@bio-logic.info

**POSTERNAK Ganna**
ENAMINE Ltd
Kyiv *(Ukraine)*
posternak.anna@mail.ru

**POUCHARD Michel**
Université Bordeaux 1, ICMCB-CNRS
Pessac *(France)*
pouchard@icmcb-bordeaux.cnrs.fr

**PRUNIER Anaïs**
ENSICAEN
Caen *(France)*
anais.prunier@ensicaen.fr

**PUSHPA PRASAD Vysakh**
Müenster University
Müenster *(Germany)*
prasadvysakh1986@gmail.com

**PYTKOWICZ Julien**
Université de Cergy-Pontoise
Cergy-Pontoise *(France)*
julien.pytkowicz@u-cergy.fr

**QING Feng-Ling**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
flq@mail.sioc.ac.cn

**RACK Michael**
Basf SE
Ludwigshafen *(Germany)*
michael.rack@basf.com

**RADAN Kristian**
Jožef Stefan Institute
Ljubljana *(Slovenia)*
kristian.radan@ijs.si

**RAPP Magdalena**
Adam Mickiewicz University
Poznan *(Poland)*
magdrapp@amu.edu.pl

**READ Roger W.**
University of New South Wales
Sydney, NSW *(Australia)*
r.read@unsw.edu.au

**REHMER Alexander**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
rehmerax@hu-berlin.de

**RESNATI Giuseppe**
Politecnico di Milano
Milano *(Italy)*
giuseppe.resnati@polimi.it

**RIEDEL Sebastian**
Albert-Ludwigs Universität Freiburg
Freiburg *(Germany)*
sriedel@psichem.de

**ROESCHENTHALER Gerd-Volker**
Jacobs University
Bremen *(Germany)*
g.roeschenthaler@jacobs-university.de

**ROESKY Herbert W.**
University of Göttingen
Göttingen *(Germany)*
hroesky@gwdg.de

**ROLANDO Christian**
Université Lille 1
Villeneuve D'Ascq *(France)*
Christian.Rolando@univ-lille1.fr

**ROLLET Anne-laure**
PECSA, Université Pierre et Marie Curie-CNRS
Paris *(France)*
anne-laure.rollet@upmc.fr

**SAKANAKA Yoshihide**
Doshisha University
Kyoto *(Japan)*
sakanaka@mail.doshisha.ac.jp

**SANSOTERA Maurizio**
Politecnico di Milano
Milano *(Italy)*
maurizio.sansotera@polimi.it

**SAVCHENKO Natalia**
Lab. of Laboratory of Fluoride Materials
Vladivostok *(Russia)*
savchenko@ich.dvo.ru

**SCHICKINGER Manuel**
Ludwig-Maximilian University
Munich *(Germany)*
Manuel.Schickinger@cup.uni-muenchen.de

**SCHMIDT Larisa**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
la_schmidt@gmx.net

**SCHMIDT Gregory**
Arkema, CRRA
Pierre Benite *(France)*
gregory.schmidt@arkema.com

**SCHROBILGEN Gary**
McMaster University
Hamilton, On *(Canada)*
schrobil@mcmaster.ca

**SELMI Ania**
Areva NC
Pierrelatte *(France)*
ania.selmi@areva.com

**SENN Remo**
ETH Zürich
Zürich *(Switzerland)*
senn@inorg.chem.ethz.ch

**SEPPELT Konrad**
FU Berlin
Berlin *(Germany)*
seppelt@zedat.fu-berlin.de

**SERGEEV Sergey**
Chemtaurus GmbH
Bremen *(Germany)*
sergey.sergeev@chemtaurus.com

**SEVERAC Romain**
DuPont France
Mantes la Jolie *(France)*
romain.severac@dupont.com

**SHAIKH Rizwan**
Universität of Muenster
Müenster *(Germany)*
rizwansh.org12@gmail.com

**SHARTS Olga**
Fluorotronics Inc.
Carlsbad, Ca *(USA)*
olgasharts@gmail.com

**SHEN Qilong**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
shenql@sioc.ac.cn

**SHIBATA Norio**
Nagoya Institute of Technology
Nagoya *(Japan)*
nozshiba@nitech.ac.jp

**SHIBATOMI Kazutaka**
Toyohashi University of Technology
Toyohashi *(Japan)*
shiba@ens.tut.ac.jp

**SHIBAYAMA Takaaki**
Central Glass Co. ltd.
Ube City *(Japan)*
takaaki.shibayama@cgco.co.jp

**SHIMIZU Yusuke**
University of Fukui
Fukui *(Japan)*
yusuke_shimizu1031@yahoo.co.jp

**SHIN Dong-Soo**
Changwon National University
Changwon, Gn *(S. Korea)*
dsshin@changwon.ac.kr

**SHINOHARA Takamichi**
Kyushu University
Fukuoka *(Japan)*
shinohara@cstf.kyushu-u.ac.jp

**SHIRYAEVA Vera**
JSC «Leading Scientific Research Institute of
Chemical Technology»
Moscow *(Russia)*
shiryaeva_vv@mail.ru

**SHTERENBERG Alexander**
Makhteshim Agan Industries
Ashdod *(Israel)*
alexander.s@agan.co.il

**ŠIMKO František**
Institute of Chemistry, Dept of Molten Salts
Bratislava *(Slovakia)*
uachsim@savba.sk

**SIMUNEK Ondrej**
Institute of Chemical Technology
Prague *(Czech Republic)*
ondrejsimunek@seznam.cz

**SINGH Rajiv**
Honeywell International
Buffalo, NY *(USA)*
Rajiv.Singh@Honeywell.com

**SKAPIN Tomaž**
Jožef Stefan Institute
Ljubljana *(Slovenia)*
tomaz.skapin@ijs.si

**SOBRIO Franck**
CNRS-CEA-Unicaen
Caen *(France)*
sobrio@cyceron.fr

**SONGWEI Lu**
PPG Industries Inc.
Monroeville *(USA)*
slu@ppg.com

**SONNENDECKER Paul**
University of Pretoria
Pretoria *(South Africa)*
paul.sonnendecker@up.ac.za

**STOCKER Wolfgang**
W.L. Gore & Associates GmbH
Munich *(Germany)*
wstocker@wlgore.com

**STREM Barbara**
Strem Chemicals Inc.
Newburyport, MA *(USA)*
barbara@strem.com

**SYVRET Robert**
Arkema Inc.
King of Prussia, Pa *(USA)*
robert.syvret@arkema.com

**TAGUCHI Takeo**
Sagami Chemical Research Institute
Tokyo *(Japan)*
taguchi@toyaku.ac.jp

**TAKAHIRA Yusuke**
Asahi Glass Co. Ltd.
Yokohama-Shi *(Japan)*
yusuke-takahira@agc.com

**TANAKA Miki**
Setsunan University
Hirakata *(Japan)*
07p189tm@edu.setsunan.ac.jp

**TARASCON Jean-Marie**
Université de Picardie Jules Verne, LRCS
Amiens *(France)*
jean-marie.tarascon@u-picardie.fr

**TARUI Atsushi**
Setsunan University
Hirakata *(Japan)*
tarui-a@pharm.setsunan.ac.jp

**STEBE Marie-José**
Université de Lorraine
Vandoeuvre-Les-Nancy *(France)*
marie-jose.stebe@univ-lorraine.fr

**STRAUSS Steven**
Colorado State University
Fort Collins, Co *(USA)*
steven.strauss@colostate.edu

**SUKACH Volodymyr**
Institute of Organic Chemistry
Kyiv *(Ukraine)*
vsukach@bigmir.net

**SZEWCZYK Marta**
Adam Mickiewicz University
Poznan *(Poland)*
martszew@amu.edu.pl

**TAKAHARA Atsushi**
Kyushu University
Fukuoka *(Japan)*
takahara@cstf.kyushu-u.ac.jp

**TALAEEMASHHADI Sadaf**
Politecnico di Milano
Milano *(Italy)*
stalaeemashhadi@chem.polimi.it

**TANAKA Hirotaka**
Kanagawa University
Hiratsuka *(Japan)*
atsutaka32@gmail.com

**TARASENKO Karen**
Institute of Bioorganic Chemistry &
Petrochemistry
Kyiv *(Ukraine)*
takaren@mail.ru

**TASAKA Akimasa**
Doshisha University
Kyoto *(Japan)*
aki_tasaka_load@yahoo.co.jp

**TAVCAR Gašper**
Jožef Stefan Institute
Ljubljana *(Slovenia)*
gasper.tavcar@ijs.si

**THANGARAJU Dheivasigamani**
ENSCP-Chimie ParisTech
Paris *(France)*
d-thangaraju@etu.chimie-paristech.fr

**THIBAUDEAU Sebastien**
Université de Poitiers-CNRS
Poitiers *(France)*
sebastien.thibaudeau@univ-poitiers.fr

**THRASHER Joseph S.**
Clemson University
Anderson, Sc *(USA)*
thrash5@clemson.edu

**TILLY Goulven**
PREVOR
Valmondois *(France)*
g.tilly@prevor.com

**TOBIAS Platen**
Clariant Produkte GmbH
Burgkichen *(Germany)*
tobias.Platen@clariant.com

**TOKUNAGA Etsuko**
Nagoya Institute of Technology
Nagoya *(Japan)*
tokunaga.etsuko@nitech.ac.jp

**TOMINA Veronika**
Chuiko Institute of Surface Chemistry
Kyiv *(Ukraine)*
v.v.tomina@mail.ru

**TRESSAUD Alain**
ICMCB-CNRS
Pessac *(France)*
tressaud@icmcb-bordeaux.cnrs.fr

**TROUCHAUD Jean**
Groupement de Génie industriel
*(France)*
trouchaud.jean@wanadoo.fr

**TERRANEO Giancarlo**
Politecnico di Milano
Milano *(Italy)*
giancarlo.terraneo@polimi.it

**THENAPPAN Alagu**
Honeywell International
Morristown *(USA)*
alagu.thenappman@honeywell.co

**THOMPSON Stephen**
University of St Andrews
St Andrews *(UK)*
st59@st-andrews.ac.uk

**TIEBES Joerg**
Bayer CropScience AG
Frankfurt-Am-Main *(Germany)*
joerg.tiebes@bayer.com

**TKACHENKO Anton**
ENAMINE Ltd
Kyiv *(Ukraine)*
anpontk@bignir.net

**TOGNI Antonio**
ETH Zürich
Zurich *(Switzerland)*
atogni@ethz.ch

**TOLMACHEVA Natalia**
ENAMINE Ltd
Kyiv *(Ukraine)*
natta_t@ukr.net

**TRAMšEK Melita**
Jožef Stefan Institute
Ljubljana *(Slovenia)*
melita.tramsek@ijs.si

**TROSTYANSKAYA Yulia**
Jacobs University
Bremen *(Germany)*
y.trostyanskaya@jacobs-university.de

**TSVETNIKOV Alexander**
Institute of Chemistry, Fluoride Materials
Vladivostok, Primorskiy *(Russia)*
tsvetnikov@ich.dvo.ru

**VALLRIBERA Adelina**
Universitat Autonoma de Barcelona
Barcelona *(Spain)*
adelina.vallribera@uab.es

**VICIC David**
Lehigh University
Bethlehem, Pa *(USA)*
dav512@lehigh.edu

**VINCENT Jean-marc**
ISM, Université de Bordeaux, CNRS
Talence *(France)*
jm.vincent@ism.u-bordeaux1.fr

**VOVK Mykhaylo**
Institute of Organic Chemistry
Kyiv *(Ukraine)*
mvovk@i.com.ua

**WAGNER Olaf**
FU Berlin
Berlin *(Germany)*
olaf.wagner@fu-berlin.de

**WLASSICS Ivan**
Solvay Specialty Polymers
Bollate, Milano *(Italy)*
ivan.wlassics@solvay.com

**WOLFS Mélanie**
Université de Nice Sophia Antipolis & CNRS
Nice *(France)*
Melanie.WOLFS@unice.fr

**XU Ping**
W. L. Gore & Associates Inc.
Elkton, Ma *(USA)*
pxu@wlgore.com

**YAJIMA Tomoko**
Ochanomizu University
Tokyo *(Japan)*
yajima.tomoko@ocha.ac.jp

**YANAI Hikaru**
Tokyo University of Pharmacy & Life Sciences
Tokyo *(Japan)*
yanai@toyaku.ac.jp

**VAN HIJFTE Nathalie**
INSA de Rouen - IRCOF
Mont-Saint-Aignan *(France)*
nathalie.van-hijfte@insa-rouen.fr

**VILLANO Massimo**
Guarniflon Spa
Castelli Calepio, Bg *(Italy)*
massimo.villano@guarniflon.com

**VINTS Inna**
Tel Aviv University
Tel Aviv *(Israel)*
innnkav@gmail.com

**WADEKAR Mohan**
Institut Charles Gerhardt
Montpellier *(France)*
mohan.wadekar@enscm.fr

**WAGNER Veit**
Jacobs University
Bremen *(Germany)*
v.wagner@jacobs-university.de

**WóJTOWICZ-RAJCHEL Hanna**
Adam Mickiewicz University
Poznan *(Poland)*
wojto@amu.edu.pl

**XIAO Ji-Chang**
Shanghai Institute of Organic Chemistry,
Shanghai *(China)*
jchxiao@sioc.ac.cn/jchxiao@gmail.com

**YAGUPOLSKII Yurii**
Institute of Organic Chemistry
Kyiv *(Ukraine)*
Yagupolskii@ioch.kiev.ua

**YAMAZAKI Takashi**
Tokyo University of Agriculture & Technology
Koganai *(Japan)*
tyamazak@cc.tuat.ac.jp

**YARUSOVA Sofia**
FEB Russian Academy of Sciences
Vladivostok *(Russia)*
yarusova_10@mail.ru

**YE Shijie**
FU Berlin
Berlin *(Germany)*
shijie.ye@fu-berlin.de

**YONEZAWA Susumu**
University of Fukui
Fukui *(Japan)*
yonezawa@matse.u-fukui.ac.jp

**ZAGGIA Alessandro**
Università degli Studi di Padova
Padova *(Italy)*
alessandro.zaggia@unipd.it

**ZAMOSTNA Lada**
Humboldt-Universität Zu Berlin
Berlin *(Germany)*
lada.zamostna@chemie.hu-berlin.de

**ZAMYSHLYAYEVA Olga**
N.I. Lobachevsky Nizhniy Novgorod State University
Nizhniy Novgorod *(Russia)*
zam.olga@mail.ru

**ZHANG Xingang**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
xgzhang@mail.sioc.ac.cn

**ZHANG Wei**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
weizhang83@sioc.ac.cn

**ZHANG Pengcheng**
university of Freiburg
Freiburg *(Germany)*
zhangpengchenggrace@hotmail.com

**ZHAO Chun-Patrick**
Sino-Rich Material Science Co. Ltd.
Beijing *(China)*
zhao.chun@sino-rich.com.cn

**ZONG Guoqiang**
Shanghai Institute of Organic Chemistry
Shanghai *(China)*
gqzong@sioc.ac.cn

# ACCOMPANYING PERSONS

**Yao AKIYAMA**
*(Japan)*

**Rachel ALTY**
*(USA)*

**Olga BROUKINA**
*(Russia)*

**Anna BUDNIKOVA**
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**Neina MEWS**
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*(Germany)*

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http://www.arkema.com/

**ARKEMA, France's leading chemicals producer**, has a long experience in research and industrial production of fluorochemicals on a global scale. Arkema's portfolio for fluoro products includes :
- HFC's (HydroFluoroCarbons) and HCFC's (HydroChloroFluoroCarbons) under the brand name Forane®, owing to its industrial experience on fluorocarbons since 1949. These products are used for the following applications:
- Refrigerants for air-conditioning, cooling applications (commercial refrigeration, buildings, automotive?) and heat pumps. Arkema has earned recognition for innovations in this field by being awarded two Société Chimique de France prizes in 10 years.
- Blowing agents for polymeric foams (polyurethane or polystyrene)
- Raw materials for fluorinated polymers
- Degreasing, cleaning or drying solvents
- PVDF (PolyVinyliDene Fluoride) under the brand name Kynar® since 1965. This polymer's high resistance makes it a material of choice for chemical processing equipments, electrical wires, and high protection metal coatings. Kynar® is used in many industries, including chemical and petrochemical industries, or in architectural applications.

Latest Arkema developments include binders for electrodes in lithium-ion batteries, photovoltaic panels and water base coating Kynar Aquatec, a "Pierre Potier Prize" winner, awarded to companies committed to sustainable development. This solvent-free grade is used as a coating for the manufacture of roofs that reflect sunlight, therefore reducing air-conditioning costs and achieving major energy savings.
- Fine chemicals catalysts for the chemical industry: $BF_3$ (Boron trifluoride) and BTFM (BromoTriFluoroMethane).

# INDUSTRIAL SILVER SPONSORS

http://www.areva.com

**AREVA** supplies solutions for power generation with less carbon. Its expertise and unwavering insistence on safety, security, transparency and ethics are setting the standard, and its responsible development is anchored in a process of continuous improvement.
Ranked first in the global nuclear power industry, AREVA's unique integrated offering to utilities covers every stage of the fuel cycle, nuclear reactor design and construction, and related services. The group is also expanding its operations to renewable energies – wind, solar, bioenergies, hydrogen and storage – to be one of the leaders in this sector worldwide.
With these two major offers, AREVA's 48,000 employees are helping to supply ever safer, cleaner and more economical energy to the greatest number of people.

http://www.bayer.com

**BAYER** is a global enterprise with core competencies in the fields of health care, agriculture and high-tech materials. Bayer CropScience, the subgroup of Bayer AG responsible for the agricultural business, has annual sales of EUR 7.255 billion (2011) and is one of the world's leading innovative crop science companies in the areas of seeds, crop protection and non-agricultural pest control. The company offers an outstanding range of products including high value seeds, innovative crop protection solutions based on chemical and biological modes of action as well as an extensive service backup for modern, sustainable agriculture. In the area of non-agricultural applications, Bayer CropScience has a broad portfolio of products and services to control pests from home and garden to forestry applications. The company has a global workforce of 21,000 and is represented in more than 120 countries. This and further news is available at: www.press.bayercropscience.com.

http://www.cea.fr/english-portalhttp://www.cea.fr/english-portal

**Commissariat à l'énergie atomique et aux énergies alternatives** – **CEA** is a French government-funded technological research organisation. A prominent player in the European Research Area, it is involved in setting up collaborative projects with many partners around the world.
Acteur majeur de la recherche, du développement et de l'innovation, le CEA intervient dans quatre grands domaines : énergies bas carbone (nucléaire et renouvelables), défense et sécurité, technologies pour l'information et technologies pour la santé.
http://www.daikin.com

**DAIKIN Industries** is the world's foremost manufacturer of fluorochemical products and is a leading expert in that field. We strive to find new possibilities for living and industry by making the most of fluorine characteristics using our own exclusively developed technologies. There are a number of early developments of alternative HFCs, fluorocarbon resins, and fluorocarbon rubber widely used in applications ranging from the data and semiconductor industries to household items used in everyday living. The potential for developing applications for these products is growing without limit for the fluorochemical industry.
A unique company, Daikin is also involved in the fields of mechanics, electronics and chemistry. While enhancing and uniting technologies of various fields, we hope to grow and develop further, actively expanding our activities on a global scale.

http://www.dupont.com/

**DuPont de Nemours** has been bringing world-class science and engineering to the global marketplace in the form of innovative products, materials, and services since 1802. The company believes that by collaborating with customers, governments, NGOs, and thought leaders we can help find solutions to such global challenges as providing enough healthy food for people everywhere, decreasing dependence on fossil fuels, and protecting life and the environment. DC&F has a diverse portfolio of high performing chemical and fluoroproducts businesses. Our heritage is innovative science and unwavering commitment to safety, stewardship and our core values.

http://www51.honeywell.com/

**HONEYWELL** is the largest producer of poly(chlorotrifluoroethylene) PCTFE in the world, used in many applications such as coatings and blisters for pharmaceuticals and medical drugs and items. Honeywell is also the producer of novel fluorinated olefins, 1234ze(E), 1234yf, 1233zd(E).

http://www.merck.fr

**MERCK** is a global pharmaceutical and chemical company with total revenues of €10.3 billion in 2011, a history that began in 1668, and a future shaped by more than 40,000 employees in 67 countries. Its success is characterized by innovations from entrepreneurial employees. Merck's operating activities come under the umbrella of Merck KGaA, in which the Merck family holds an approximately 70% interest and free shareholders own the remaining approximately 30%. In 1917 the U.S. subsidiary Merck & Co. was expropriated and has been an independent company ever since. Within Merck Performance Materials, a chemical platform based on Ionic Liquids has been established which are used for a wide variety of applications. A special focus is laid on fluorinated hydrophobic anions such as the FAP-anion.

http://www.solvayplastics.com/

**SOLVAY SPECIALITY POLYMERS** is a leading global producer of innovative materials which consistently surpass the highest standards for sustainability, durability, chemical and temperature resistance, weatherability and transparency. Its high-performance polymers include fluoropolymers, fluoroelastomers, sulfone polymers, semi-aromatic polyamides and specialty polyethylenes, which fulfill critical requirements of global customers involved in industries such as the Automotive, Aerospace, Chemical, Healthcare, Membranes, Plumbing, Semiconductor, Oil & Gas, Wire & Cable and Alternative Energy ones. Expert in Fluoropolymers, Solvay Specialty Polymers produces thermoplastics, elastomers and thermoplastics elastomers (Tecnoflon trademark). Thanks to its broad portfolio which include more than 30 brands available in over 1,500 formulations, and a powerful combination of technological innovation and close customer collaboration, Solvay Specialty Polymers is committed to providing sustainable solutions that contribute to improving quality of life.

# INDUSTRIAL BRONZE SPONSORS

http://www.3M.com/

**3M** Company is a diversified technology company that sells over 50.000 products worldwide. 3M started started in 1902 with the manufacture of sandpaper , a product that consists of various layers. Refinement of the precision coating created one of 3M's most important technology platforms , resulting in the first self adhesive tapes . Today 3M is capable of placing minuscule objects in exact order on substrates , for many applications. This led to new retro-reflective materials and abrasives . Current main activities of 3M are in the fields of health care , display enhancement and graphic solutions , electronics,electrical and telecommunications ,safety and security systems ,automotive and aerospace applications , abrasive systems , filtration ,tapes and adhesives and products for the office, home and leisure.

Activities in fluorotechnologies are focussing on fluoropolymers , fluorinated fluids and surface active agents and their applications .

Innovation is a key feature of 3M . It invest about 6% of its sales into research & development , realising 30% of its turnover with products that did not exist four years earlier.

http://212.172.204.219/abcrestore/

**abcr** supplies specialty chemicals to renowned pharmaceutical and chemical companies worldwide. Through our logistics centre in Karlsruhe, we organise and manage the distribution of products to more than 10,000 laboratories. The expertise and technical support provided by our chemists and engineers, together with short delivery times, have made us a “preferred supplier” for many customers. Our products are available in regular catalogue units, as well as on a semi-bulk and bulk scale. You will have access to a wide range of organic and inorganic fine chemicals, precious metal compounds, fluorochemicals, organometallics, organosilanes, silicones, homogeneous and heterogeneous catalysts, phosphines, rare earth compounds, and many more.
http://www.sigmaaldrich.com

**Sigma-Aldrich** is a leading life science and high technology company. Our chemical and biochemical products and kits are used in scientific research, biotechnology, pharmaceutical development, the diagnosis of disease, and as key components in high technology manufacturing. The Company’s committed workforce of 7,700 employees in 40 countries accelerates our customers’ success through innovative products, customized solutions and unsurpassed service.
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http://www.apolloscientific.co.uk

**APPOLO SCIENTIFIC** is currently celebrating twenty years of supplying intermediate and building block compounds into the research and development sector. We specialise in supplying fluorinated compounds and currently have in excess of 15000 listed, in a range which now consists of over 50000 compounds - including our non-fluorinated intermediates, rapidly expanding biochemicals portfolio, inorganics listing, deuterated solvents and other spectroscopy consumables. In our own UK laboratories we manufacture fluorochemicals and key heterocyclic building blocks in quantities from just a few grams to over 50kg.
Apollo has recently become wholly owned by Central Glass, in Japan, and works closely with it’s Central Glass corporate partners: Synquest Laboratories (USA) who specialise in fluorine aliphatic compounds and gas handling and Central Glass Germany who undertake API and intermediate production at their cGMP certified facility, whilst also utilising the availability of semi-bulk to commercial production sites within Japan.

http://www.basf.com

**BASF**, The Chemical Company - We create chemistry for a sustainable future. We combine economic success, social responsibility and environmental protection.
Through science and innovation we enable our customers in almost all industries to meet the current and future needs of society.

http://www.cgco.co.jp/

**Central Glass Group** manufactures a variety of organic and inorganic fluorinated fine chemicals, using hydrogen fluoride synthesized from fluorite ($CaF_2$) or high-purity fluorine produced through electrolysis of hydrogen fluoride. We provide stably high quality products through integrated production from materials to products. We are proud that the quality of our products receives high commendation from our overseas clients, as well as from users in Japan. The Central Glass Group positively responds to diverse needs of the electronics, pharmaceutical and agrochemical industries and also puts its energies in the fluorinated fine chemicals business toward development of new products fulfilling emerging needs.

http://www.enamine.net/

Since its foundation in 1991, **ENAMINE** has been meeting the increasing and varying demands of the market for novel diverse compounds via high throughput screening. The company has been strategically investing a lot of resources in the synthesis of building blocks for its own inventory. The latter eventually allowed taking the lead in synthesis of novel compound libraries. Today Enamine possesses the world's largest collection of screening compounds exceeding 2 million pure samples stored as dry powders. Each year over 150,000 new compounds are added to our collection for our repeated clients' satisfaction. Continuous and increasingly important production of building blocks required for synthesis of compound libraries and fine medicinal chemistry resulted in creation of another Enamine commercial catalogue. It's not surprising that after the screening collection, the related catalogue of building blocks turned out to be the largest in the world. To benefit from the latest scientific findings in medicinal chemistry, we welcome to board on our integrated discovery programs, including computer-aided drug design, biomolecular and ADME/Tox screening, medicinal chemistry in hit-to-lead and lead optimization phases.

www.fluorochem.co.uk

**FLUOROCHEM** has been supplying fluorinated intermediates for R & D for over 45 years. In that time our product range has expanded to almost 100000 items and now includes not only fluorinated materials but many novel organic intermediates. We offer fluorinating agents, heterocyclics, boronic acids, and an ever-increasing catalogue of novel and competitively priced fluorine containing molecules.

http://www.hydroquebec.com/fr/index.html

**Hydro-Québec** generates, transmits and distributes electricity. It uses mainly renewable generating options, in particular large hydro, and supports the development of other technologies—such as wind energy and biomass. A responsible corporate citizen committed to sustainability, Hydro-Québec carries out construction projects to prepare for the future. It also conducts R&D in energy-related fields, including energy efficiency.

http://www.micromeritics.com/

**Micromeritics** manufactures automated particle characterization analytical laboratory instruments for R&D, QA/QC, production, and process control applications. Characteristics determined include: particle size, surface area,pore volume, pore size, pore size distribution, absolute density, envelope density, bulk density, catalytic activity, and active surface area.
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*www.groupeseb.com*

With operations in almost 150 countries, **Groupe SEB** is today the world leader in Small Household Equipment. Group SEB accounts 25 000 employees and generated a 4 billion euro turnover in 2012. It has earned strong positions on all continents through a wide, diversified product range and an exceptional brand portfolio (KRUPS, MOULINEX, TEFAL, ROWENTA, LAGOSTINA, ALL-CLAD). A pioneer accustomed to leading the way, Groupe SEB has based its strategy on innovation. Creating value, innovation drives its growth and is the key to its international success.

http://www.sino-rich.com.cn

**Beijing SINO-RICH** is a leading innovative fluorinated materials and functional fluopolymer coatings manufacture in China which dedicate to provide state of art of cross linkable fluoropolymer and its coating for energy storage, solar cell, heat reflection, ceramic hybrid non-stick, anti-graffiti, anti-fouling, dry lubrication, durable weathering as well as de-ice application.

http://www.f-techinc.co.jp

**TOSOH F-TECH, INC**. is an expert in the field of fluorinated organic compounds and their derivatives. TOSOH F-TECH has made dramatic technological breakthroughs, including but not limited to a patented process for the production of 2,2,2-Trifluoroethanol (TFEA), a unique continuous gas phase technology for Trifluoromethyl Iodide ($CF_3I$), and the commercialization of Trifluoromethyl Uracil (TFU) derivatives.

http://www.unimatec.co.jp/index.html
http://http://www.unimatec-europe.com/english/homepage.html

**UNIMATEC CO.,LTD** is a manufacturer of high performance rubber polymers (NoxtiteÂ®) and chemical specialty products based on advanced Fluorine-and Organic chemistry. CheminoxÂ® UNIMATEC is manufacturing fluorinated monomers, telomers and fluorinated specialities. Those are the building blocks for Fluoropolymers, Hydrophobation Oleophobation agents, fluorinated crosslinkers and a line of fluoro agents and intermediates.
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http://www.fluoridearc.com/

**Advance Research Chemicals, Inc. (ARC)** was founded in 1987 by Dr. Dayal T. Meshri who is recognized internationally for his pioneering work of 50 years in fluorine chemistry. From its modest beginnings of two employees in a 3000 square feet research chemical house, ARC has grown into one of the premier specialty fluorine companies in the world. In just 25 years, ARC has expanded to over 85 employees, utilizing 250,000 square feet of production area.

www.bio-logic.info

**Bio-Logic** is a French company created in 1983 based in the French Alps near Grenoble city. Bio-Logic develops and manufactures high end potentiostats/ Galvanostats and Multipotentiostats for more than 15 years. Bio-logic provides integrated EIS systems, either in multichannels format for battery cyclers or single portable potentiostats. Our EC-Lab software platform proposes all kind of DC and AC electrochemical tests procedure with all the calculations tools integrated. Our leadership in the energy testing is balanced by our ability to explore low current as well. Our company is manufacturing other products like scanning systems (SECM, LEIS) and in the Rapid Kinetics area (stopped flow) for30 years. We have sister Companies in USA and India completed by a distribution network in Asia and Europe. At this time, the corporate office in France employs 50 people.
http://www.equilabo.com/

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http://www.strem.com/

**STREM CHEMICALS**, established in 1964, manufactures and markets over 4,000 metals, inorganics, organometallics and nanomaterials for R&D in academic institutions and in the pharmaceutical, microelectronics, chemical and petrochemical industries. Custom synthesis work is also provided. cGMP manufacturing is available. Products include metal catalysts and ligands for organic synthesis(chiral), MOCVD/ALD precursors, metal carbonyls, metal-based nanoparticles and more

www.sudfluor.com

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SUDFLUOR also develops innovation programs involving Fluorine Science for a sustainable Environment and welcomes collaborations with academic and industrial Researchers. *Contact: info@sudfluor.com*

www.specificpolymers.fr

**SPECIFIC POLYMERS** (SP) is a private company created in 2003 with a turnover of 500 K€ (2012) with 10 employees. The company is located in Montpellier (France). SP acts as a R&D service provider in the field of monomers and polymers bearing hetero elements (fluorine, phosphorus, silicon, sulfur, nitrogen) and/or functional groups.
**SP offers a broad catalogue of functional monomers and polymers (more than 500 chemicals sold to 200 customers in 20 countries) designed by/from SP, carrying out the scale-up and industrial development. These monomers/polymers are intended for several applications (aeronautics, automotive (tyres, coatings, gaskets), biomaterials, cosmetics, energy (fuel cell, lithium battery, photovoltaics), environment (water treatment, gas recovery), pharmaceutics, etc.**

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