Journal of Fluorine Chemistry 134 (2012) 8–10

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Preface

Fluorine is an omnipresent chemical element in our everyday life. The last two decades have witnessed a spectacular growth of interest in selectively fluorinated molecular compounds. Nowadays, several hundreds of thousands molecules contain at least one fluorine atom. These molecules found essential applications in life sciences, medicine, pharmacology, medical imaging, agricultural chemistry, materials, etc. The manifold facets of fluorinated biomaterials and drugs are illustrated by examples ranging from inorganic ceramics to perfluorinated organic molecules. The applications include neuroleptics, anti-cancer, antibiotics, PET imaging for an early detection of tumors, etc. In the cornerstone field of energy storage and conversion, fluorine constitutes a key-element because most devices devoted to the storage of the energy (lithium-ion batteries, fuel cells) use fluoride materials as electrodes, electrolytes containing a fluoride salt, fluoromembranes, etc. Another illustration is the impact of this element in the nuclear cycle *via* the synthesis of uranium hexafluoride which is an unavoidable step toward uranium enrichment. Through these examples, it is clear that whatever its state, fluorine has a significant societal impact.

In France, in the Henri Moissan's trail, the research in the field of fluorine chemistry has been traditionally important, as well in organic as in polymeric, or inorganic chemistry. The applied aspects of fluoride products have been also largely developed since the discovery of this element. Nowadays, several industrial groups are key-players of the World Fluorine Chemistry. The major activities related to F-element of the most important industry groups located in France are given below, together with addresses and contacts.

Until the creation of the French Fluorine Network, researchers involved in the fluorine chemistry developed their activities without the assistance of a federative structure capable of making the interface not only between the various involved laboratories but also, and especially, between the academic and industrial worlds. In 2002, the first steps for the creation of *French National Network on Fluorine Chemistry* were undertaken under the aegis of the Chemistry Department (now Institute of Chemistry) of CNRS (National Center for Scientific Research). The main objective of the network is to identify clear scientific orientations which could have an important societal impact, in particular in terms of public health and to recommend the implementation and the development of interdisciplinary works. Thus, its first vocation is to promote the activities connected to fluorine and fluoride-based products in the varied sectors of chemistry and new technologies (energy control, electronics and opto-electronics, life sciences, environment (for instance CFC substitutes, green chemistry, etc.)). Today, about forty laboratories belong to the network, in which the scientific animation is insured through five thematic sectors:

1. methodology in organic synthesis, catalysis,
2. methodology in inorganic chemistry and materials science,
3. polymers and surfactants; physical chemistry and modeling; surface treatments,
4. fluorine and life sciences,
5. fluorine, energy and new technologies.

For additional information about the *French National Network in Fluorine Chemistry*, we suggest the reader to visit the network website (http://www.reseau-fluor.fr/).

1. Major industrial activities related to F-element in France

Arkema [1], a key-player of the world chemistry, the first French chemist, has a long experience in the search and the production of molecules and fluoride materials at the world level. Their activity range includes:

- HFC (hydrofluorocarbons) and HCFC (hydrochlorofluorocarbons) marketed under the brand Forane®, related to a long industrial experience of fluorocarbons, dating back 1949. They are intended for various uses: refrigerants for the refrigeration and the air-conditioning (business, building, automobile); expansion agents for the manufacturing of polymer foams (polyurethanes and polystyrene); raw materials for the manufacturing of fluoropolymers; solvents for degreasing, cleaning or drying.
- Boron trifluoride (BF_3) and bromotrifluoromethane (BTFM), fine chemistry products, used as catalysts in the chemical industry.
- PVDF (polyvinyldifluoride) marketed under the brand Kynar®, regularly manufactured since 1965. The product is used in numerous industries such as chemical industry, petroleum industry or buildings. Its high strength makes of this polymer a coating or a key-material for chemical engineering, electric cable-manufacturing, high protection coating for metallic surfaces. Among the last Kynar's applications, we can quote electrodes of lithium-ion batteries, photovoltaic panels, or roofing. Kynar Aquatec® without solvent allows to realize covers of roofs reflecting the solar radiation, with long life expectancy, and contributing to a sustainable air conditioning and the energy-efficiency of the buildings. This product received in 2010 the "*Pierre Potier Award*", a prize dedicated to innovative companies in the field of the sustainable development.

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Major player of the conversion of uranium at the international level, Comurhex [2], a subsidiary of Areva company, transforms, in several stages, the mining uranium concentrate into uranium hexafluoride. The first stage of conversion of "yellow cake" concentrate into uranium tetrafluoride is realized by acidic dissolution followed by hydrofluorination at the Malvési plant. In the Pierrelatte plant, uranium tetrafluoride is converted into hexafluoride (UF_6) by contact of gaseous fluorine with powdered UF_4 at high-temperature in a flame reactor. So, being gaseous at 65 °C, (UF_6) can be enriched (as ^{235}U) by gaseous diffusion or by centrifugation. Besides enriched UF_6, that is further transformed into nuclear fuel, depleted hexafluoride is transformed into oxide in a defluorination plant which is the only one worldwide to realize this type of process at the industrial scale. F_2-gas, the raw material required for the conversion process is continuously produced by electrolysis of KH_2F_3 in HF medium.

Since the first half of the twentieth century, DuPont [3] has been a significant contributor to advances in fluorine chemistry. This long history has led to a variety of products such as fluorinated gases (refrigeration, air conditioning, etc.), fluoropolymers (plastic materials or coatings with high chemical and thermal resistance such as polytetrafluoroethylene, PTFE), or fluorotelomers (unique surface properties). Fluorotelomers are short perfluorinated chains attached to an ethylene spacer that when coupled to a polar group yield a fluorinated surfactant. The polymerization of a monomer (e.g., acrylate) containing fluorotelomer functionality yields a comb-shaped fluorinated polymer with a hydrocarbon backbone. The "tines" of the comb contain the fluorotelomer functionality. These fluorinated polymers are utilized as oil and water repellent impregnating agents for textiles, leather or construction materials. Fluoropolymers and fluorotelomer-based polymers that meet specific end-use performance requirements when incorporated into articles (e.g., non-stick cookware, clothing) may qualify for Teflon® brand certification. In 2002, DuPont acquired Elf Atochem's fluorotelomer operations. With this acquisition, DuPont now operates a modern plant in France that produces fluorotelomer-based surfactant and polymeric products. Building upon decades of Elf Atochem research at the Pierre Bénite and Levallois-Perret sites, the DuPont technology group develops new products and processes at a state of the art R&D and Technical Service laboratory established in 2003, 40 miles outside of Paris. New short chain surfactants and polymeric products marketed under the trade name Capstone® are developed here in collaboration with DuPont's global R&D center located in Wilmington, Delaware.

Fluorination process during fuel tank blow molding is currently developed by INERGY Automotive Systems [4], consisting in the treatment of monolayer HDPE parts using a mixture of fluorine and nitrogen in order to lower the permeability of these parts to hydrocarbon vapours. Fluorination increases the quality of the barrier properties of the automotive fuel tanks to fuel and makes the polyethylene less permeable to gasoline fuel by modifying the polymer surface.

The difluorinated semi-synthetic vinca alkaloid derivative, vinflunine ditartrate, manufactured at Laboratoires Pierre Fabre [5] has been approved in Europe since 2009 in the treatment of cancer of the gall bladder. Further clinical trials are in progress to assess its efficacy in the treatment of breast cancer. The discovery of this novel compound through a collaboration between the French pharmaceutical group, Pierre Fabre Médicament, and the French national research agency, the CNRS, has been well documented (Fahy et al., J. Amer. Chem. Soc. 119 (1997) 8576; Jacquesy et al., J. Fluor. Chem. 114 (2002) 139). Super-acid conditions (HF/SbF_5) were used to introduce two fluorine atoms into a region of the bis indole skeleton that had previously proved inaccessible, resulting in a significant modification of the pharmacological properties of the molecule. A key challenge in the development of this molecule was the establishment of a safe and robust manufacturing process for the supply of material to support clinical trails and commercial launch. This challenge was met and the compound is currently manufactured with a validated process under cGMP conditions at the Pierre Fabre Médicament facility at Gaillac, north of Toulouse.

Since July 2010, Rhodia Group [6] is organized around 11 global business units (GBU). The Aroma Performance Global Business Unit (GBU), part of Rhodia's consumer chemicals cluster, includes the diphenol and fluorinated intermediates operations, comprising three main market segments: aroma ingredients, inhibitor solutions and crop protection, health and specialties. Fluorine chemistry is based on core technologies that Rhodia masters since several years in its Salindres plant, and is the heart of the portfolio and innovations of the crop protection health and specialties segment. Rhodia Aroma Performance has developed a unique range of chemical intermediates for pharmaceuticals and agrochemicals. Based on its expertise in gas and liquid fluorination technologies, Rhodia offers the largest portfolio of fluoroaliphatics building blocks: trifluoroacetic acid and triflic acid derivatives, manufactured combining environmentally sustainable and competitive integrated processes. Rhodia is proposing new key compounds in the electronic industry, a fast growing market. Rhodia is the only player integrated through the whole trifluoroacetic acid–potassium trifuoromethanesulfinate–triflic acid chain. A recently launched product rapidly gaining importance is LiTFSI, a fluorinated lithium salt that can be used in antistatic applications, in batteries or, with other cations than Li, as powerful and promising Lewis acid catalyst. Rhodia has proprietary methods to produce difluoroacetic acid and derivatives, key building blocks used in a new family of agrochemical and pharmaceutical blockbusters, in which the Company aims to become worldwide leader. Continuously striving to offer to its customers new molecules allowing to get innovative properties, Rhodia Aroma Performance is developing a new product family based on dilfuoromethane-sulfonylchloride chemistry, which could be the molecule of tomorrow.

From fluorspar to functionalized polymers – Solvay Fluor, a Division of Solvay Chemicals [7], integrates the activities of fluorochemistry of the group. Products are made worldwide in about ten plants. The application range extends from hydrofluoroalcanes used as refrigerants, foaming, or precision solvent agents to special reagents for the electronics such as F_2, C_4F_6, COF_2. The ethylene monofluorocarbonate is used as additive in the electrolytes of Li-ion batteries. SF_6 serves as an insulating gas in the electric installations of middle and high voltages. Several fluoroaluminosilicates have revolutionized the brazing of aluminium parts, and organic intermediates serve as source of fluorine for the pharmaceutical and agrochemical industries.

Among the products that are commercialized by Solvay Solexis, a Division of Solvay Plastics [8], one of the world leaders in fluoromaterials, we can quote:

- Various types of perfluoropolyethers used as lubricants, surface treatment agents, heat transfer reagents.
- Fluoro- and perfluoroelastomers particularly adapted to the severe conditions of the aeronautical, spatial industries, and resist to high thermal and chemical constraints.
- A wide range of fluoride coatings based on either amorphous or crystalline copolymers, for high chemical and thermal strengths.
- Fluoride copolymers entering the composition of membranes for fuel cells and batteries.
- Various types PTFE.

Two recent companies which are dedicated to the synthesis of new fluoro-products can be also quoted:

Innov'Orga [9] is a chemical company specialized in the field of fluorine organic chemistry, working essentially on the search and development of new fluorinated organic building blocks. The introduction of fluorine atoms in molecules is obtained *via* different techniques: nucleophilic or electrophilic direct fluorination, nucleophilic trifluoromethylation, electrophilic trifluoromethylation, etc.

Specific Polymers [10] have been developing the synthesis of functionalized fluorinated monomers and polymers. These new products can be used for various properties: low refraction index, thermostability, hydrophoby and oleophoby. The applications range includes aeronautics, cosmetics, electronics, energy, pharmacy, surface treatments, etc.

The aim of this special issue is to highlight the high level of activities of French laboratories involved in Fluorine Sciences, through papers in which, after a brief presentation of the current activity of each group in the field of Fluorine Chemistry, original results recently obtained will be presented. We do hope that after reading this special issue, you will be convinced that research in this particular field of Chemistry is very active in France on both academic and industrial sides.

References

[1] Contact: ARKEMA, CRRA, Rue Henri Moissan, BP63, 69493 Perre Bénite Cedex, France, web: http://www.arkema.com/.
Gérard Guilpain (gerard.guilpain@arkema.com) Directeur Centre de Recherche Rhône Alpes.

[2] Contact Comurhex-Areva, BP 29, 26701 Pierrelatte Cedex, France, web: http://www.areva.com/FR/activites-761/.
Bertrand Morel (bmorel@comurhex.fr) R&D Manager.

[3] Contact DuPont, Chemicals and Fluoroproducts, Geneva, Switzerland
Martial Pabon (Martial.Pabon@che.dupont.com) R&D, Regulatory and Product Stewardship Manager.

[4] Contact: INERGY Automotive Systems, 92, rue du Maréchal Leclerc, Venette – BP 80259, 60202 Compiègne Cedex, France, web: www.inergyautomotive.com.
Wilfried Lemasson (wilfried.lemasson@inergyautomotive.com), System Architecture & Component Europe.

[5] Contact: Institute de Recherche Pierre Fabre, 16, Rue Rostand B.P.92, 81603 Gaillac, France, web: http://www.pierre-fabre.com/.
Paul Hellier (paul.hellier@ pierre-fabre.com) Responsable Développement Industriel.

[6] Contact: Rhodia, CRTL, St Fons, 69
François Metz (francois.metz@eu.rhodia.com) Senior Staff Scientist, Centre de Recherches et de Technologies de Lyon.

[7] Contact: Solvay Fluorés France, 25, Rue de Clichy, F-75442 Paris Cedex 09, France, web: www.solvay-fluor.com; e-mail: Solvay-Fluores-France@solvay.com.

[8] Contact: Solvay SOLEXIS, 25, Rue de Clichy, F-75442 Paris Cedex 09, France, web: www.solvayplastics.com; e-mail: solvaysolexis.information@solvay.com.

[9] Contact: Innov'orga, Faculté des Sciences, Moulin de la Housse, BP 1039, 51 687 Reims, France,
Sonia Gouault-Bironneau or Sophie Goumain (contact@innovorga. com).

[10] Contact: Specific Polymers, Avenue de l'Europe, Cap Alpha, 34830 Clapiers, France
Cedric Loubat (cedric.loubat@specificpolymers.fr) R&D manager.

Henri Groult*
Université P. & M. Curie, Case 51, Laboratoire PECSA, UMR 7195, 4 place Jussieu, Bât. F74, 75005 Paris, France

Alain Tressaud
ICMCB, CNRS, Université Bordeaux I, 87, Av. Dr A. Schweitzer, 33608 Pessac Cedex, France

*Corresponding author
E-mail address: henri.groult@upmc.fr (H. Groult).

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Preface

Henri Groult, Alain Tressaud

Université P. & M. Curie, Case 51, Laboratoire PECSA, UMR 7195, 4 place Jussieu, Bât. F74, 75005 Paris, France
ICMCB, CNRS, Université Bordeaux I, 87, Av. Dr A. Schweitzer, 33608 Pessac Cedex, France

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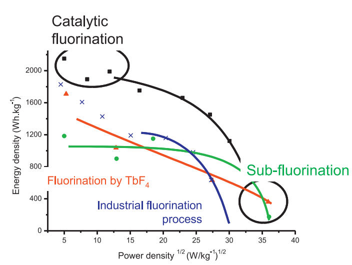
Applicative performances of fluorinated carbons through fluorination routes: A review

Katia Guérin, Marc Dubois, Axel Houdayer, André Hamwi

Clermont-Université, Laboratoire des Matériaux Inorganiques, UMR CNRS 6002-Université Blaise Pascal, 24 av. des Landais, 63171 Aubière Cedex, France



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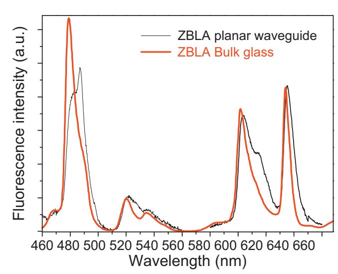
Fluoride and oxyfluoride glasses for optical applications

V. Nazabal[a], M. Poulain[a], M. Olivier[a], P. Pirasteh[a], P. Camy[b], J.-L. Doualan[b], S. Guy[c], T. Djouama[e], A. Boutarfaia[d], J.L. Adam[a]

[a]*Sciences Chimiques de Rennes, UMR-CNRS 6226, Equipe Verres et Céramiques, Université de Rennes1, 35042 Rennes, France*
[b]*CIMAP, ENSI Caen, 6 boulevard du Maréchal Juin, 14050 Caen cedex 4, France*
[c]*Laboratoire de Physico-Chimie des Matériaux Luminescents (LPCML), UMR-CNRS 5620, Université Claude Bernard-Lyon 1, Villeurbanne, France*
[d]*Laboratoire de Chimie Appliquée, Université M. Khider, 07000 Biskra, Algeria*
[e]*Laboratoire d'Électronique Quantique, Faculté de Physique, USTHB. BP 32, El-Alia 16111, Alger, Algeria*



doi:10.1016/S0022-1139(12)00011-5

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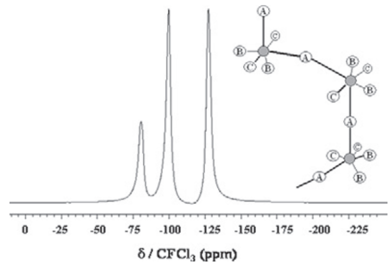
Investigation of the purity of antimony pentafluoride using ^{19}F NMR

A. Bock[ab], M. Dubois[ab], P. Bonnet[ab], A. Hamwi[ab], D. Avignant[ab], L. Moch[c], B. Morel[c]

[a]*Clermont Université, Université Blaise Pascal, Laboratoire des Matériaux Inorganiques, 63171 Aubière, France*
[b]*CNRS, UMR 6002, 63170 Aubière, France*
[c]*Comurhex BP No. 29, 26701 Pierrelatte, France*



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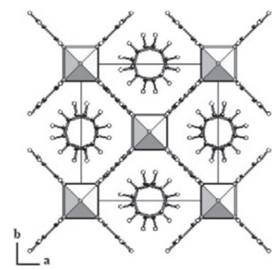
Mixed metal^{II}–metal^{IV} hybrid fluorides

Jérôme Lhoste, Karim Adil, Armel Le Bail, Marc Leblanc, Annie Hémon-Ribaud, Vincent Maisonneuve

Laboratoire des Oxydes et Fluorures, UMR CNRS 6010, Faculté des Sciences et Techniques, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex 09, France

Six type II mixed metal hybrid fluorides are obtained under solvothermal conditions assisted by microwave heating. The structures are determined either from single crystal or powder X-ray diffraction data.



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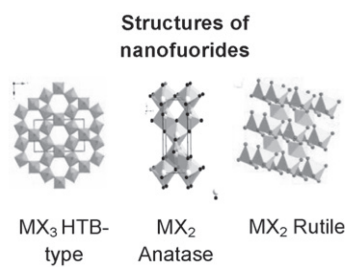
About MX_3 and MX_2 (M^{n+} = Mg^{2+}, Al^{3+}, Ti^{4+}, Fe^{3+}; X^{p-} = F^-, O^{2-}, OH^-) nanofluorides

A. Demourgues, N. Penin, D. Dambournet, R. Clarenc, A. Tressaud, E. Durand

Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Université Bordeaux, 87, Avenue du Dr. A. Schweitzer, 33608 Pessac Cedex, France

Mg, Al, Ti and Fe-based nanofluorides with high surface area, containing mixed anions (F^-, O^{2-}, OH^-) and adopting HTB, anatase and rutile frameworks have been prepared by solvothermal routes and the structures have been determined.



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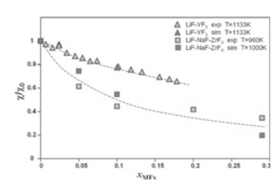
Structural effects on the electrical conductivity of molten fluorides: Comparison between LiF–YF_3 and LiF–NaF–ZrF_4

Anne-Laure Rollet, Mathieu Salanne, Henri Groult

UPMC Univ Paris 06, CNRS, ESPCI, Laboratoire PECSA, 4 place Jussieu, 75005 Paris, France

The electrical conductivity of molten alkali fluoride mixtures with ZrF_4 and YF_3 was determined from impedance experiments and molecular dynamics simulations. An important decrease was observed and analyzed in terms of the local structure of the multivalent metallic species.



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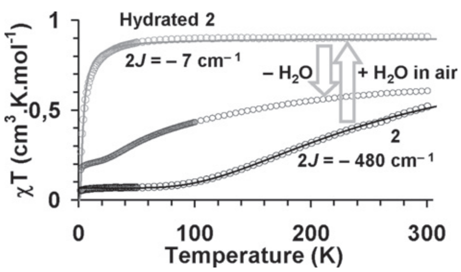
A fluorous copper(II)–carboxylate complex which magnetically and reversibly responds to humidity in the solid state

Artur Motreff[a], Rosenildo Correa da Costa[a], Hassan Allouchi[b], Mathieu Duttine[c], Corine Mathonière[c], Carole Duboc[d], Jean-Marc Vincent[a]

[a]*Université de Bordeaux, Institut des Sciences Moléculaires (CNRS-UMR 5255), Talence, France*
[b]*Université de Tours, Laboratoire de Chimie Physique (PCMB-E.A 4244), Tours, France*
[c]*CNRS, Université de Bordeaux, ICMCB, 87 av. du Dr Schweitzer, 33608 Pessac, France*
[d]*Université Joseph Fourier, Département de Chimie Moléculaire (CNRS-UMR 5250), Grenoble, France*



The fluorous dimeric copper(II)–carboxylate complex $[Cu_2(C_8F_{17}CO_2)_4(acetone)_2]$ (2) magnetically and reversibly responds to humidity in the solidstate

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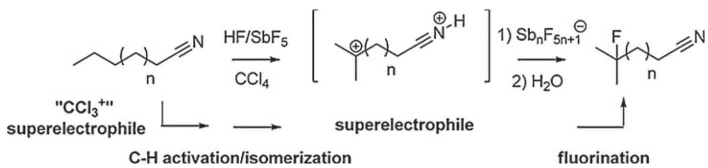
Dications in superacid HF/SbF_5: When superelectrophilic activation makes possible fluorination and/or C–H bond activation

Agnès Martin-Mingot[a], Guillaume Compain[a], Fei Liu[a], Marie-Paule Jouannetaud[a], Christian Bachmann[b], Gilles Frapper[b], Sébastien Thibaudeau[a]

[a]*Université de Poitiers, UMR 6514, Laboratoire "Synthèse et Réactivité des Substances Naturelles", 40 Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*
[b]*Université de Poitiers, UMR 6503, Laboratoire de Catalyse en Chimie Organique, 40 Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*

The reactivity of aliphatic amides/ketones/imines and nitriles was studied in superacid HF/SbF5 in the presence of CCl4. After the identification of the reaction intermediates by in situ NMR experiments, we propose that the sp3C–H bond functionalization (fluorination) by the superacid system is strongly dependant on the superelectrophilic character of the distonic dicationic intermediates.



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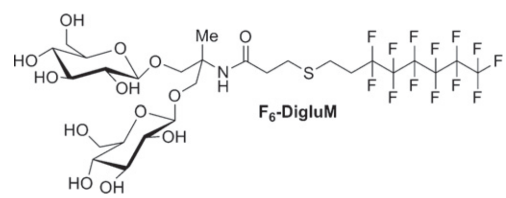
A diglucosylated fluorinated surfactant to handle integral membrane proteins in aqueous solution

Maher Abla[a], Grégory Durand[ab], Cécile Breyton[cde], Simon Raynal[ab], Christine Ebel[cde], Bernard Pucci[ab]

[a]*Université d'Avignon et des Pays de Vaucluse, Equipe Chimie Bioorganique et Systèmes Amphiphiles, 33 rue Louis Pasteur, F-84000 Avignon, France*
[b]*Institut des Biomolécules Max Mousseron (UMR 5247), 15 avenue Charles Flahault, F-34093 Montpellier Cedex 05, France*
[c]*CEA, Institut de Biologie Structurale (IBS), F-38027 Grenoble, France*
[d]*CNRS, UMR 5075, IBS, Grenoble, France*
[e]*Université Joseph Fourier - Grenoble 1, IBS, Grenoble, France*

The synthesis of F6-DigluM is based on a one-pot reduction/alkylation of a fluorinated thioacetate onto an acrylamido-type polar head precursor, using $NaBH_4$/methanol under reflux. F6-DigluM exhibits a critical micellar concentration of 0.4 mM and forms small and well-defined globular micelles. The homogeneity and the stability of bacteriorhodopsin solubilised in F6-DigluM were observed.



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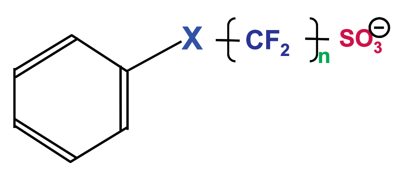
Polymer electrolytes based on new aryl-containing lithium perfluorosulfonates

E. Paillard[a], F. Toulgoat[b], C. Iojoiu[c], F. Alloin[c], J. Guindet[c], M. Medebielle[d], B. Langlois[d], J.Y. Sanchez[c]

[a]*University of Münster, Institut für Physikalische Chemie, Corrensstraβe 28/30, 48149 Münster, Germany*
[b]*UMR UDS/CNRS 7200, Faculté de Pharmacie Strasbourg, 74 route du Rhin, BP. 24, 67401 Illkirch, France*
[c]*UMR 5246 ICBMS, Bâ timent Raulin, Université Claude Bernard Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne cedex, France*
[d]*LEPMI, UMR 5279 CNRS – G-INP, UJF, UdS, BP. 75, 38402 Saint-Martin-d'Hères cedex, France*

The paper gathers new results obtained from a series of aryl-containing lithium perfluorosulfonates dissolved in a macromolecular solvent i.e. poly(oxyethylene). The anion syntheses starting from an aryl sulphide or an aryl ketone, a variety of new salts can be designed by changing the nature of the aryl moiety.



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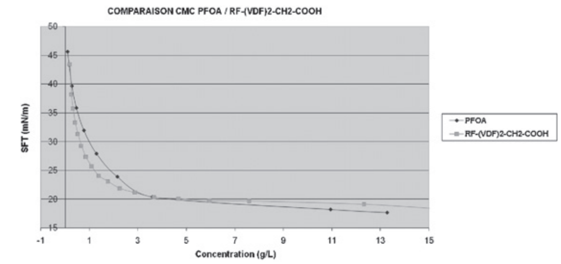
New fluorinated surfactants based on vinylidene fluoride telomers

G. Boutevin[a], D. Tiffes[a], C. Loubat[a], B. Boutevin[b], B. Ameduri[b]

[a]*Specific Polymers, Avenue de l'Europe–Cap Alpha, 34830 Clapiers, France*
[b]*Ingénierie et Architectures Macromoléculaires, UMR (CNRS) 5253, Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France*



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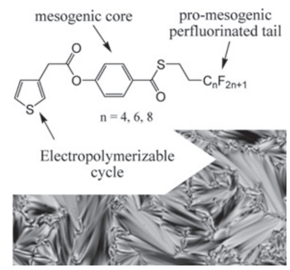
Synthesis, characterization and surface wettability of polythiophene derivatives containing semi-fluorinated liquid-crystalline segment

Thierry Darmanin, Elisabeth Taffin de Givenchy, Sonia Amigoni, Frédéric Guittard

Université de Nice – Sophia Antipolis, Laboratoire Chimie des Matériaux Organiques et Métalliques, Equipe chimie organique aux interfaces, Parc Valrose, 06108 Nice Cedex 2, France

Original semi-fluorinated liquid crystalline monomers, containing a single phenyl unit as mesogenic core linked to a thiophene moiety, potentially usable for the construction of efficient anti wetting surfaces by electro-copolymerization.



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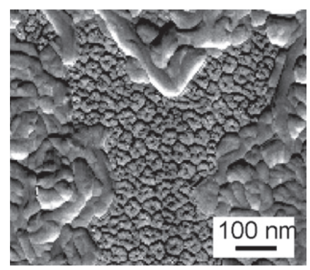
Strasbourg's SOFFT team—Soft functional systems self-assembled from perfluoroalkylated molecular components

Marie Pierre Krafft

Systèmes Organisés Fluorés à Finalités Thérapeutiques (SOFFT), Institut Charles Sadron (CNRS UPR 22), Université de Strasbourg, 23 rue du Loess, 67034 Strasbourg Cedex 2, France

The SOFFT team focuses on the design, synthesis, investigation and potential applications of self-assembled functional fluorinated molecular systems. Here is a multilayered thin surface film with discrete and continuous layers of self-assembled (F-alkyl)alkyl diblocks.



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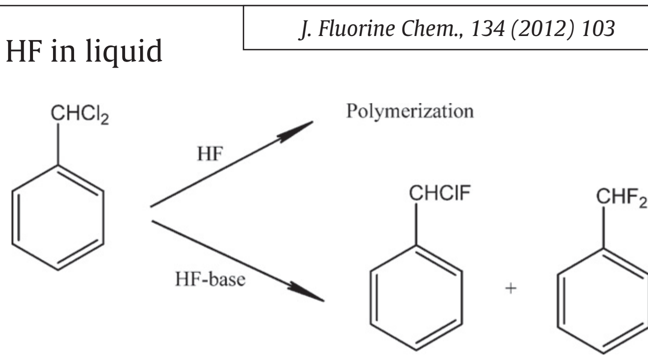
Catalytic fluorination of dichloromethylbenzene by HF in liquid phase. Preparation of fluorinated building blocks

Alexandre Piou, Stephane Celerier, Sylvette Brunet

Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Université de Poitiers Faculté des Sciences Fondamentales et Appliquées 40, Avenue du Recteur Pineau 86022, Poitiers cedex, France

The selective fluorination by successive Cl/F exchanges of the dichloromethylbenzene, was studied in the presence of HF as the fluorinating agent. The influence of the presence of a catalyst or a basic solvent (such as dioxane, pyridine, tributylphosphate) in order to favour the fluorination was investigated.



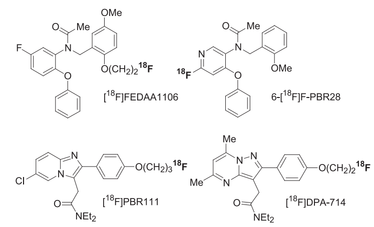
J. Fluorine Chem., 134 (2012) 107

Synthesis of fluorine-18-labelled TSPO ligands for imaging neuroinflammation with Positron Emission Tomography

Dirk Roeda, Bertrand Kuhnast, Annelaure Damont, Frédéric Dollé

CEA, Institut d'imagerie biomédicale, Service Hospitalier Frédéric Joliot, 4 place du Général Leclerc, F-91401 Orsay, France

[^{18}F]FEDAA1106, 6-[^{18}F]F-PBR28, [18F]PBR111 and[^{18}F]DPA-714 are four selected fluorine-18 labelled radioligands produced in our laboratory for imaging the translocator protein 18 kDa with Positron Emission Tomography. Various aspects of fluorine-18-radiochemistry, such as radiotracer design rationales, radioisotope production and [18F] fluoride activation, radiofluorination procedures, purification and formulation are addressed based on these structures.



J. Fluorine Chem., 134 (2012) 115

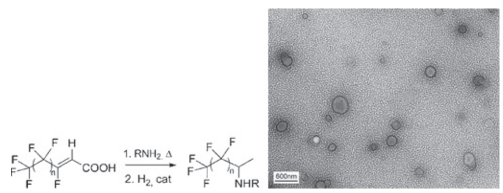
Synthesis and self-assembling behavior of F-amphiphilic functionalized amines

Nicolas Dupuy[a], Andreea Pasc[a], Estelle Mayot[a], Sedat Cosgun[b], Christine Gérardin-Charbonnier[a]

[a]*LERMaB, EA 4370, IFR 110, Faculté des Sciences et Technologies, Université Henri Poincaré, Nancy, BP 70239, 54506 Vandoeuvre-lès-Nancy, France*

[b]*Department of Chemistry, Fatih University, Istanbul, Turkey*

A very simple and efficient access to novel fluorinated/hydrogenated secondary amines, starting from commercially available fluorinated acids and a variety of primary hydrogenated amines, is described. By combining a rigid fluorinated hydrophobic tag and a flexible ethylenoxide moiety, one can design original monocatenar lipids, which are able to spontaneously form vesicles in water.

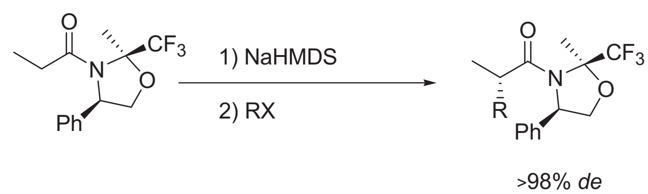


J. Fluorine Chem., 134 (2012) 122

2-Trifluoromethyl-2-methyl-4-phenyloxazolidine: A new chiral auxiliary for highly diastereoselective enolate alkylation

Arnaud Tessier, Julien Pytkowicz, Thierry Brigaud

Université de Cergy-Pontoise, Laboratoire SOSCO, F-95000 Cergy-Pontoise, France



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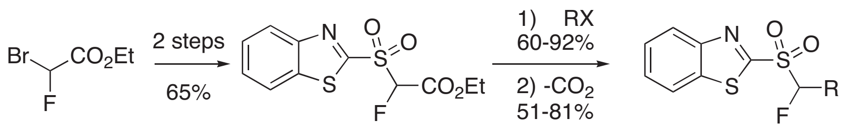
Decarboxylation of fluorosulfones for the preparation fluoroalkylidene precursors

Florent Larnaud[ab], Emmanuel Pfund[a], Bruno Linclau[b], Thierry Lequeux[a]

[a]*Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507 & FR3038, ENSICAEN, Université de Caen Basse-Normandie, 6 boulevard du Maréchal Juin, 14050, Caen, France*

[b]*School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK*

Krapcho decarboxylation of benzothiazolylsulfones opens up an improved route for the synthesis of fluorosulfones as Julia–Kocienski reagents



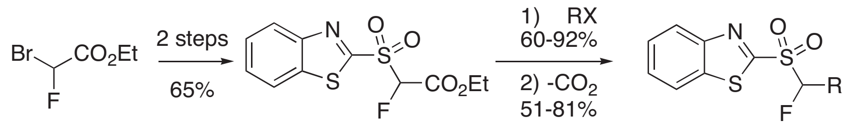
J. Fluorine Chem., 134 (2012) 136

Synthesis and evaluation of fluorinated analogues of monoamine reuptake inhibitors

Christine Philippe, Julia Kaffy, Thierry Milcent, Danièle Bonnet-Delpon

Laboratoire BioCIS-CNRS, Faculté de Pharmacie, Univ Paris-Sud, Rue J. B. Clément, F-92296 Châ tenay-Malabry,

Two series of fluorinated analogs of monoamines reuptake inhibitors have been synthesized through the incorporation of fluorinated organometallic reagents. Their binding affinities have been determined on different monoamine transporters.

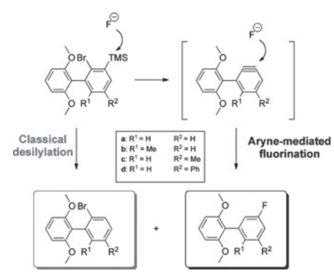


J. Fluorine Chem., 134 (2012) 146

Aryne-mediated fluorination: Synthesis of fluorinated biaryls *via* a sequential desilylation–halide elimination–fluoride addition process

Vincent Diemer, Juan Sanz Garcia, Frédéric R. Leroux, Françoise Colobert

CNRS/Université de Strasbourg (ECPM), UMR 7509, 25 Rue Becquerel, F-67087 Strasbourg Cedex 2, France

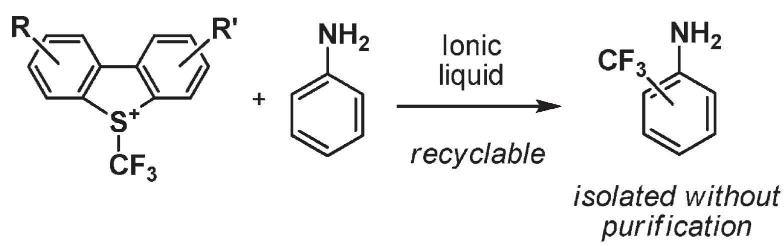


J. Fluorine Chem., 134 (2012) 156

Ionic liquids as new media for electrophilic trifluoromethylation reactions

Bruce Pégot, Yohan Macé, Céline Urban, Patrick Diter, Jean-Claude Blazejewski, Emmanuel Magnier

Institut Lavoisier de Versailles (ILV), UMR CNRS 8180, Université de Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France



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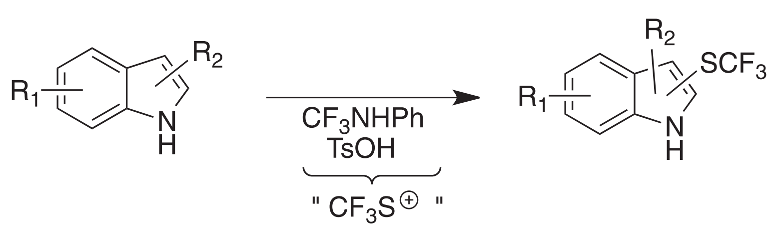
Electrophilic trifluoromethanesulfanylation of indole derivatives

Aurélien Ferry[a], Thierry Billard[a], Eric Bacqué[b], Bernard R. Langlois[a]

[a]*Université de Lyon, Université Lyon 1, CNRS ICBMS (UMR CNRS 5246) – Laboratoire SURCOOF, 43 Bd du 11 novembre 1918, Bat Chevreul, F-69622 Villeurbanne, France*

[b]*Sanofi-Aventis S.A. 136, Quai Jules Guesde, BP 14, 94403 Vitry-Sur-Seine Cedex, France*

Electron-rich aromatic compounds, in particular indoles, were trifluoromethanesulfanylated by trifluoromethanesulfanylamides under acidic activations.



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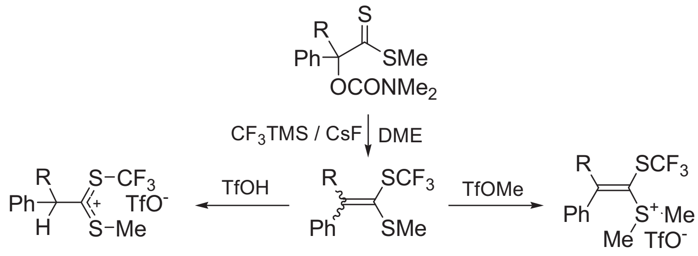
Thiophilic nucleophilic trifluoromethylation of α-substituted dithioesters. Access to *S*-trifluoromethyl ketene dithioacetals and their reactivity with electrophilic species

Sonia Gouault-Bironneau, Vadim M. Timoshenko, Fabienne Grellepois, Charles Portella

Institut de Chimie Moléculaire de Reims, Université de Reims-Champagne-Ardenne – CNRS (UMR 6229), UFR Sciences, BP 1039, 51687 REIMS Cedex 2, France

α-Dimethylcarbamoyldithioesters react with CF_3TMS under fluoride activation to lead to the title compounds. The latter are methylated at sulfur, and protonated at carbon. The corresponding salts are characterized.



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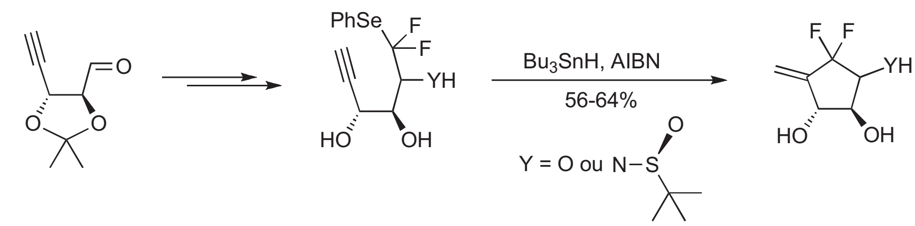
Synthesis of *exo*-methylenedifluorocyclopentanes as precursors of fluorinated carbasugars by 5-*exo*-dig radical cyclization

Gaëlle Fourrière, Eric Leclerc, Jean-Charles Quirion, Xavier Pannecoucke

Université et INSA de Rouen, CNRS, UMR 6014
C.O.B.R.A. – IRCOF, 1 rue Tesnière, 76821 Mont Saint-Aignan Cedex, France



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Towards chemical libraries based on heterocyclic scaffolds with monofluorinated and difluoroalkyl side chains

Pierre Bannwarth[a], Danielle Grée[a], Saibal Das[b], Jhillu Singh Yadav[b], René Grée[a]

[a]*Université de Rennes 1, Laboratoire Sciences Chimiques de Rennes CNRS UMR 6226 and Laboratoire Chimie et Photonique Moléculaires CNRS UMR 6510, Avenue du Général Leclerc, 35042 Rennes Cedex, France*
[b]*Organic Chemistry Division I, Indian Institute of Chemical Technology, 500607 Hyderabad, India*

Focused chemical libraries of heteroaromatic systems with mono- and gemdifluoroalkyl side chains have been prepared. Starting from corresponding scaffolds, Pd-catalyzed reactions have been performed, including by automated procedures, to afford libraries of molecules designed for biological applications.