3 | 9 August 2025

ESFC LISBON

21st European Symposium on Fluorine Chemistry

BOOK OF ABSTRACTS

EMAIL

esfc.lisbon@chemistry.pt

WEBSITE

21-esfc-lisbon.events.chemistry.pt

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Book of Abstracts

21st European Symposium on Fluorine Chemistry

ESFC LISBON 2025

Lisbon, 3 – 9 August 2025

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Welcoming Message

Dear Colleagues,

On behalf of the Organising Committee, we welcome you to the 21st European Symposium on Fluorine Chemistry in Lisbon, Portugal.

The European Symposium on Fluorine Chemistry (ESFC) brings together industrial and academic fluorine chemists from around the world and was first held in Munich in 1965. The conference is held every three years in Europe, and the event and scientific program cover all topics related to fluorous technologies and fluorine chemistry.

The 21st European Symposium on Fluorine Chemistry will be held in Lisbon, Portugal, hosted by the NOVA School of Science and Technology and LAQV/REQUIMTE in partnership with the Portuguese Society of Chemistry (SPQ). The ESFC LISBON will bring together large numbers of international researchers from academia, research institutes, and industry. The scientific program offers forums that encompass a wide range of applied and fundamental fluorine chemistry. It will offer insights from physical and theoretical chemistry, as well as the fields of fluorous technologies, sustainable processes, biomedicine, and materials science, among others.

We look forward to an outstanding program filled with engaging scientific discussions, as well as the opportunity for you to experience the rich history, vibrant culture, and natural beauty of Lisbon and Portugal.

The 21st ESFC Chairs:

Ana B. Pereiro
LAQV/REQUIMTE, NOVA School of Science and Technology (NOVA FCT), NOVA University Lisbon, Portugal

João M. M. Araújo
LAQV/REQUIMTE, NOVA School of Science and Technology (NOVA FCT), NOVA University Lisbon, Portugal

History of the European Symposium on Fluorine Chemistry

The European Symposium on Fluorine Chemistry, established in 1965, is an academic conference held every three years that focuses on fluorine chemistry. Although hosted in Europe, the event traditionally attracts researchers from across the globe. Its scientific program encompasses all aspects of fluorine chemistry pertinent to both fundamental and applied research.

01	1965	Munich (West Germany)	*Friedrich Weygand*
02	1968	Göttingen (West Germany)	*Oskar Glemser*
03	1970	Aix-en-Provence (France)	*Paul Hagenmuller, Pierre Plurien*
04	1972	Ljubljana (Yugoslavia)	*Jože Slivnik*
05	1974	Aviemore (Scotland)	*David Sharp*
06	1977	Dortmund (West Germany)	*Martin Schmeiser*
07	1980	Venice (Italy)	*Giampaolo Gambaretto*
08	1983	Jerusalem (Israel)	*Henry Selig*
09	1989	Leicester (United Kingdom)	*Raymond D. Peacock*
10	1992	Padua (Italy)	*GianPaolo Gambaretto*
11	1995	Bled (Slovenia)	*Boris Žemva*
12	1998	Berlin (Germany)	*Konrad Seppelt, Dieter Lentz*
13	2001	Bordeaux (France)	*Alain Tressaud*
14	2004	Poznan (Poland)	*Henryk Koroniak*
15	2007	Prague (Czech Republic)	*Oldřich Paleta*
16	2010	Ljubljana (Slovenia)	*Tomaž Skapin, Melita Tramšek, Boris Žemva*
17	2013	Paris (France)	*Henri Groult, Bruno Améduri, Alain Tressaud*
18	2016	Kiev (Ukraine)	*Valeriy Kukhar, Yuriy Shermolovich, Yurii Yagupolskii*
19	2019	Warsaw (Poland)	*Wojciech Grochala, Henryk Koroniak (honorary)*
20	2022	Berlin (Germany)	*Thomas Braun, Sebastian Riedel*
21	**2025**	**Lisbon (Portugal)**	***Ana B. Pereiro, João M. M. Araújo***
22	2028	Prague (Czech Republic)	*Petr Beier*
23	2031	...	

General Information: Lisbon

Lisbon was awarded by the World Travel Awards as Europe's Leading City Destination 2024. It is the capital of Portugal and a historical city full of stories to tell, where the sun shines 290 days a year and the temperature rarely drops below 15 ˚C. A city where you feel safe wandering around day or night, where the cuisine is dedicated to creating over a thousand ways to cook the beloved ***bacalhau*** (salted cod), and where you will find hotels and restaurants to suit every taste, budget and requirement. Discover Lisbon, a city full of authenticity where old customs and ancient history intermix with cultural entertainment and hi-tech innovation. Lisbon is ageless, but it loves company, as you will find out if you meet someone and ask them to explain, with lots of gestures and repetition, where the best place is to listen to ***Fado***. After all, Lisbon is famous for its hospitality and the family-like way it welcomes visitors.

Please find further information about Lisbon's top attractions, events, restaurants, hotels and more on this official website: https://www.visitlisboa.com/.

Time Zone: The time zone in Lisbon is WEST (summer) and GMT (winter).

Water: Tap water in Portugal is safe drinking water!

Electricity: Standard voltage is 220V AC. Plugs are European style with two round pins.

Currency, Banks and Post Offices: The national currency in Portugal is the Euro. Banks are open from Monday to Friday between 8:30 a.m. and 3 p.m. Post offices are usually open between 8:30 a.m. and 6 p.m. Exchange houses operate every day between 9 a.m. and 1 p.m. and from 2 p.m. to 7 p.m.

Committees

Conference Chairs

Ana B. Pereiro and João M. M. Araújo

LAQV/REQUIMTE, NOVA School of Science and Technology (NOVA FCT), NOVA University Lisbon, Portugal

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ROYAL SOCIETY OF CHEMISTRY

gradiva

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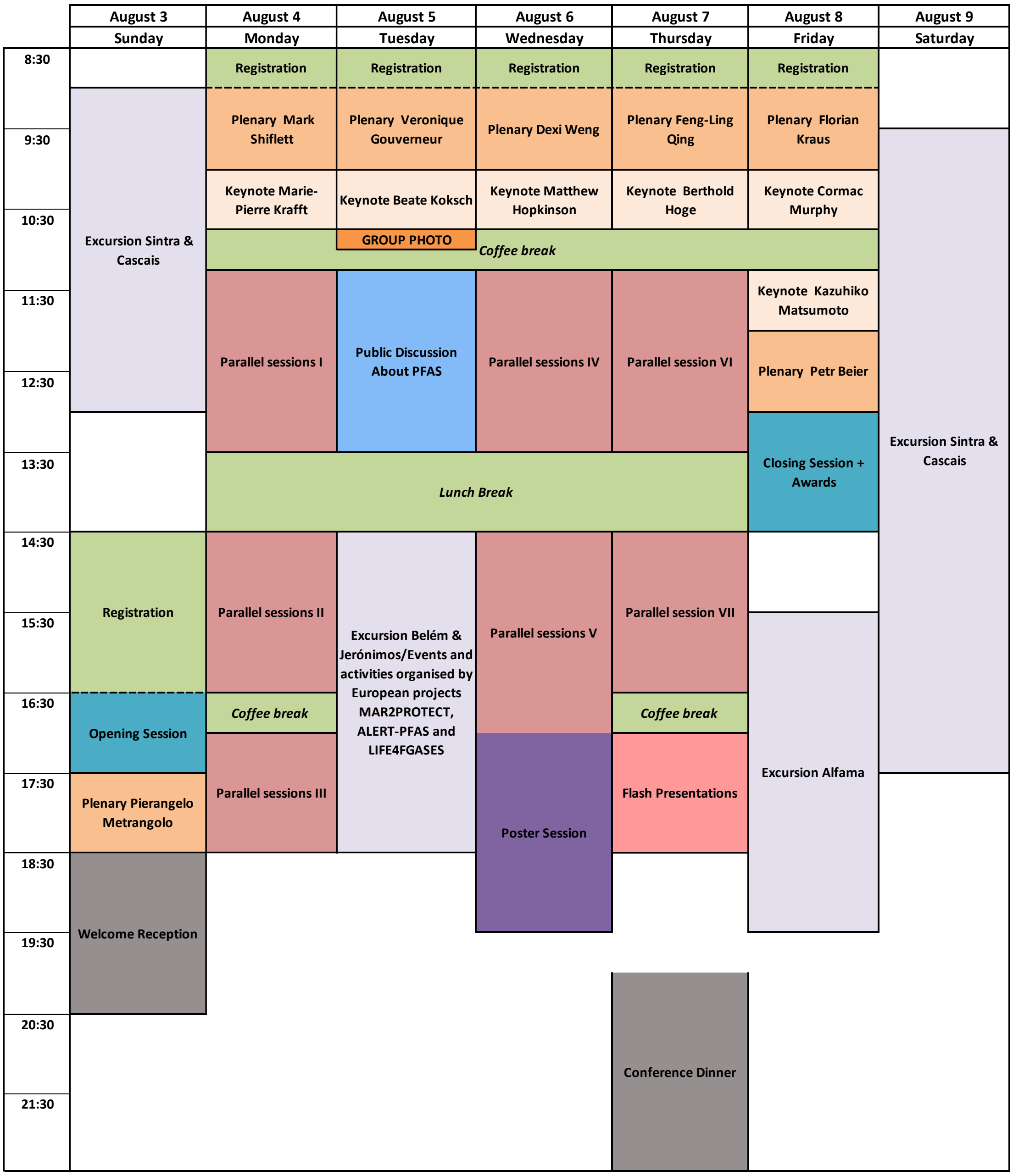
Symposium Programme Overview



	August 3 Sunday	August 4 Monday	August 5 Tuesday	August 6 Wednesday	August 7 Thursday	August 8 Friday	August 9 Saturday
8:30	Excursion Sintra & Cascais	Registration Plenary Mark Shiflett	Registration Plenary Veronique Gouverneur	Registration Plenary Dexi Weng	Registration Plenary Feng-Ling Qing	Registration Plenary Florian Kraus	
9:30		Keynote Marie-Pierre Krafft	Keynote Beate Koksch	Keynote Matthew Hopkinson	Keynote Berthold Hoge	Keynote Cormac Murphy	Excursion Sintra & Cascais
10:30		*Coffee break* Parallel sessions I	GROUP PHOTO *Coffee break* Public Discussion About PFAS	*Coffee break* Parallel sessions IV	*Coffee break* Parallel session VI	*Coffee break* Keynote Kazuhiko Matsumoto	
11:30						Plenary Petr Beier	
12:30						Closing Session + Awards	
13:30		*Lunch Break*	*Lunch Break*	*Lunch Break*	*Lunch Break*		
14:30	Registration	Parallel sessions II	Excursion Belém & Jerónimos/Events and activities organised by European projects MAR2PROTECT, ALERT-PFAS and LIFE4FGASES	Parallel sessions V	Parallel session VII		
15:30						Excursion Alfama	
16:30	Opening Session	*Coffee break* Parallel sessions III		Poster Session	*Coffee break* Flash Presentations		
17:30	Plenary Pierangelo Metrangolo						
18:30	Welcome Reception						
19:30					Conference Dinner		
20:30							
21:30							

Programme Summary

Sunday, August 3, 2025			Room
9:00	13:00	Excursion Sintra & Cascais	-
14:30	18:30	Registration	Pavilion 3
16:30	18:30	Opening Session	Auditorium II
17:15	18:15	Plenary Session - Pierangelo Metrangolo	Auditorium II
18:30	20:30	Welcome Reception	In front of Auditorium II

Monday, August 4, 2025			Room
8:30	18:30	Registration	Pavilion 3
9:00	10:00	Plenary Session - Mark Shiflett	Auditorium II
10:00	10:45	Keynote Session - Marie-Pierre Krafft	Auditorium II
10:45	11:15	Coffee Break & Exhibition	Pavilion 3
11:15	13:30	Parallel sessions I (see program)	
13:30	14:30	Lunch Break	
14:30	16:30	Parallel sessions II (see program)	
16:30	17:00	Coffee Break & Exhibition	Pavilion 3
17:00	18:30	Parallel sessions III (see program)	

Tuesday, August 5, 2025			Room
8:30	18:30	Registration	Pavilion 3
9:00	10:00	Plenary Session - Veronique Gouverneur	Auditorium II
10:00	10:45	Keynote Session - Beate Koksch	Auditorium II
10:45	10:50	Group Photo	Stairs between Auditorium II and Pavilion 3
10:50	11:15	Coffee Break & Exhibition	Pavilion 3
11:15	13:30	Public Discussion About PFAS	Auditorium II
13:30	14:30	Lunch Break	
14:30	18:30	Excursion Belém & Jerónimos/ Events and activities organised by European projects MAR2PROTECT, ALERT-PFAS and LIFE4FGASES	Pavilion 3

Wednesday, August 6, 2025			Room
8:30	18:30	Registration	Pavilion 3
9:00	10:00	Plenary Session - Dexi Weng	Auditorium II
10:00	10:45	Keynote Session - Matthew Hopkinson	Auditorium II
10:45	11:15	Coffee Break & Exhibition	Pavilion 3
11:15	13:30	Parallel sessions IV (see program)	
13:30	14:30	Lunch Break	
14:30	17:15	Parallel sessions V (see program)	
17:15	19:30	Poster Session	Pavilion 3

Thursday, August 7, 2025			Room
8:30	18:30	Registration	Pavilion 3
9:00	10:00	Plenary Session - Feng-Ling Qing	Auditorium II
10:00	10:45	Keynote Session - Berthold Hoge	Auditorium II
10:45	11:15	Coffee Break & Exhibition	Pavilion 3
11:15	13:30	Parallel sessions VI (see program)	
13:30	14:30	Lunch Break	
14:30	16:30	Parallel sessions VII (see program)	
16:30	17:00	Coffee Break & Exhibition	Pavilion 3
17:00	18:30	Flash Presentations (see program)	Auditorium II
20:00	23:00	Conference Dinner	Restaurant SUD

Friday, August 8, 2025			Room
8:30	13:30	Registration	Pavilion 3
9:00	10:00	Plenary Session - Florian Kraus	Auditorium II
10:00	10:45	Keynote Session - Cormac Murphy	Auditorium II
10:45	11:15	Coffee Break & Exhibition	Pavilion 3
11:15	12:00	Keynote Session - Kazuhiko Matsumoto	Auditorium II
12:00	13:00	Plenary Session - Petr Beier	Auditorium II
13:00	14:30	Closing Session + Awards	Auditorium II
15:30	19:30	Excursion Alfama	-

Saturday, August 9, 2025		
9:30	17:30	Excursion Sintra & Cascais

Venue and Maps

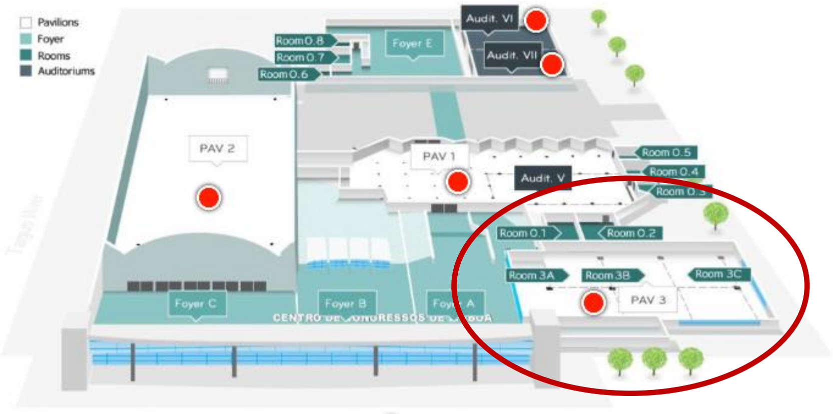
The Lisbon Congress Centre (CCL) is located next to the Tagus River, close to the historic and cultural heritage area of Belém, just a few minutes from the city centre. This area benefits from a wide range of transport options, and it is a welcoming space to carry out congresses, conferences, business meetings, fairs, parties, exhibitions and other events.

Address:

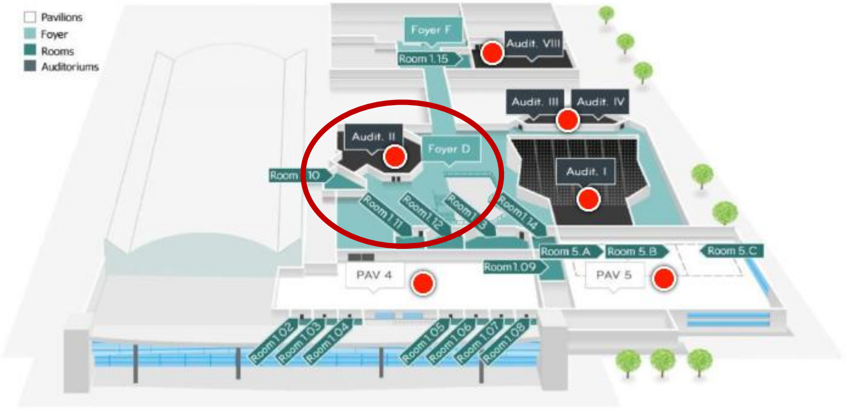
Praça das Industrias, 1

1300-307 Lisbon, Portugal

GROUND FLOOR | Pavilion 3, Rooms 3A, 3B and 3C



FIRST FLOOR | Auditorium II



Technical Information

WIFI

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LECTURES

Length

Plenary Lecture | PL | 60 min

Keynote | KN | 45 min

Invited Lecture | IL | 20 min

Oral communication | Oral | 15 min

Flash presentation | FP | 5 min

Please help keep our conference programme on schedule by adhering to these time limits.

Delivery of data for presentations

Please prepare your PowerPoint presentations in 16:9 format and submit them to email esfc.lisbon@chemistry.pt before the start of the conference. Alternatively, you may deliver them in person in the designated presentation room, no later than the session preceding your own.

POSTER SESSION

Wednesday, August 6th, 2025 | 17:15 – 19:30

Room: Pavilion 3

Posters can be mounted from the morning of August 6th. The poster session of the 6th will be accompanied by a light dinner. The posters will be **exhibited from August 6th to August 8th**. Each poster has been assigned a number, which will also be displayed on the movable wall. Our friendly ESFC LISBON staff will be on hand to assist you in finding your designated poster spot and will provide mounting material as well as assistance. Please remember to remove your posters at the end of the conference.

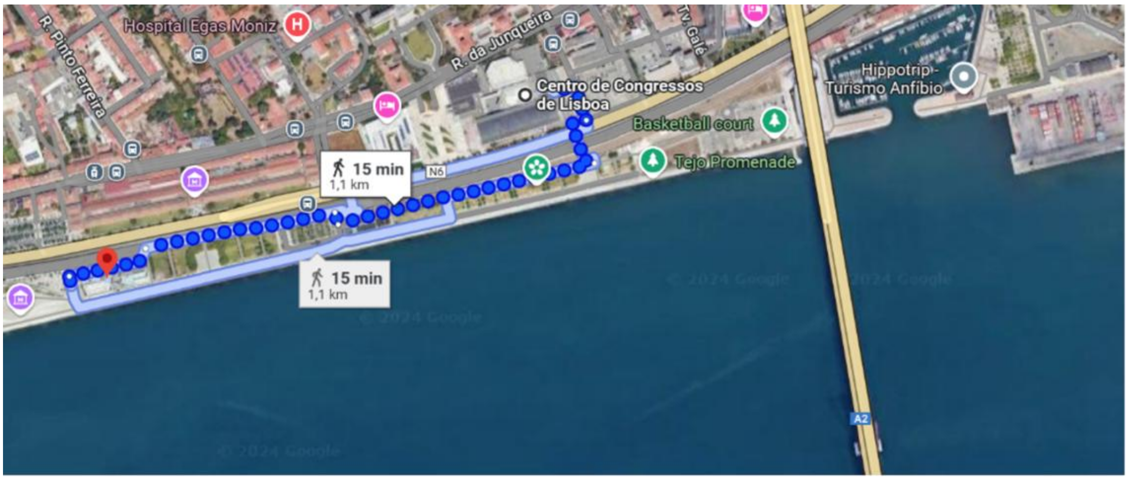
SOCIAL PROGRAMME

Welcome Reception | Sunday, August 4th, 2025 | 18:30 – 20:30

After gathering in Auditorium II for the opening session and the first plenary lecture of ESFC LISBON 2025, we will move to the welcome reception that will take place **in front of Auditorium II**.

Conference Dinner | Thursday, August 7th, 2025 | 20:00 – 23:00

The Conference Dinner will be held at the **SUD Lisboa Hall**. Situated in the iconic Belém district of Lisbon, this venue seamlessly blends modernity, sophistication, and innovation, ensuring every event is truly one of a kind. Just a 15-minute walk from the conference venue (CCL), it offers a scenic riverside route with breathtaking views of Lisbon's stunning 25th of April Bridge.



Group Photo

Tuesday, August 5th, 2025 | 10:45 – 10:50

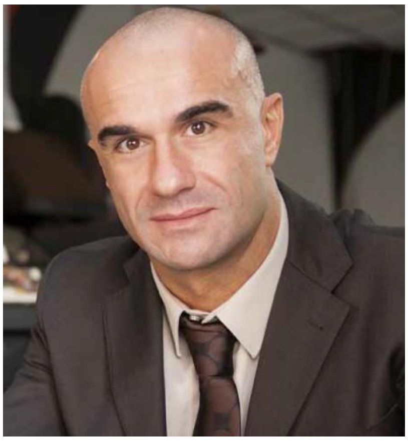
The group photograph is scheduled for Tuesday, August 5th at 10:45 **on the stairs between Auditorium II and Pavilion 3**.

Plenary Speakers

Short Biography & Abstracts

Pierangelo Metrangolo

Politechnico di Milano, Italy



Pierangelo Metrangolo is full professor of chemistry at the Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta" of Politecnico di Milano, Italy, where he is also Rector's Delegate for Sport Activities. He is also Affiliate Member at the International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM2) of the Hiroshima University in Japan. His awards include the 2005 "G. Ciamician" medal of the Italian Chemical Society, the 2005 Journals Grant Award of the Royal Society of Chemistry, the 2009 IUPAC Young Chemist Award, the Fluorous Technologies Award 2019, and the 2021 "G. Modena" medal of the Italian Chemical Society, among others. He is currently the Immediate Past-President of the Physical and Biophysical Chemistry Division (I) of the IUPAC. He is also Co-Editor of Acta Crystallogr. B (IUCr), and member of the Editorial Advisory Boards of Cryst. Growth Des. (ACS), the J. Fluorine Chem. (Elsevier), and Sci. Rep. (Nature). He is co-author of 280 international peer-reviewed publications with 26182 citations (H-index: 69) and holds 6 granted patents and 11 patent applications. In 2013 and 2018 he received two grants from the European Research Council for studying the relevance of biomolecular halogen bonds. His research interests include nanomedicine, green chemistry and sustainable development, supramolecular chemistry, crystal engineering, fluorine chemistry and biomimetic materials. In particular, his work focuses on the study of the self-assembly properties of halogenated hydrocarbons and their interactions with biomolecules for applications in the field of functional materials, environmental chemistry, and nanomedicine.

Mark Shiflett, Wonderful Institute for Sustainable Engineering, University of Kansas, USA

Mark B. Shiflett is a Distinguished Foundation Professor in the Department of Chemical and Petroleum Engineering at the University of Kansas (KU). He is the director of the new National Science Foundation Engineering Research Center – EARTH, which stands for Environmentally Applied Refrigerant Technology Hub. He is also the director of the Wonderful Institute for Sustainable Engineering at KU and the Editor-in-Chief for the Journal of Ionic Liquids. He is also cofounder and Chief Science Officer for two companies, Icorium Engineering Company and Pvera Tech, LLC. Professor Shiflett joined KU as a Foundation Professor in August 2016 after retiring from the DuPont Company. Professor Shiflett worked for DuPont for 28 years and was a Technical Fellow in the Central Research and Development organization which is located at the Experimental Station in Wilmington, Delaware. Professor Shiflett was also an adjunct professor at the University of Delaware in the Department of Chemical and Biomolecular Engineering. Professor Shiflett received his Ph.D. and M.S. degrees in chemical engineering from the University of Delaware in 2001 and 1998. He received his B.S. degree in chemical engineering from N.C. State University in 1989. Professor Shiflett is an inventor on 48 U.S. patents and has published 150 articles with over 10,000 citations on his research in both academia and DuPont. He was awarded the DuPont Bolton Carothers award in 2005, the ACS Hero of Chemistry award in 2006, and the University of Delaware presidential citation in 2007 for his development of hydrofluorocarbon refrigerant mixtures to replace chlorofluorocarbons, which were linked to the depletion of the Earth's ozone layer. Professor Shiflett was elected in 2014 to be a Fellow in the American Institute of Chemical Engineers, in 2016 to be a Division Fellow in the American Chemical Society, and in 2018 to be a Fellow in the National Academy of Inventors for his significant professional accomplishments and contributions to the chemical engineering profession. Professor Shiflett received the American Institute of Chemical Engineers Institute award for Industrial Research in 2016 for the development of non-ozone-depleting refrigerants, which have led to the healing of the Earth's ozone layer, new applications using ionic liquids, and mentoring and educating chemical engineers. Professor Shiflett is a licensed professional engineer in the State of Delaware and his research at KU focuses on developing sustainable processes and products. To learn more about Professor Shiflett and his research group you can visit their website: ***https://shiflettresearch.com*****.**

Veronique Gouverneur,

University of Oxford, UK

Véronique Gouverneur secured a PhD in chemistry at the Université Catholique de Louvain (LLN, Belgium) under the supervision of Prof. L. Ghosez. In 1992, she moved to a postdoctoral position with Prof. R. Lerner at the Scripps Research Institute (California, USA). She accepted a position of Maître de Conférence at the University Louis Pasteur in Strasbourg (France); during this period, she worked with Dr C. Mioskowski and was Associate Member of the "Institut de Science et d'Ingénierie Supramoléculaires" led by Prof. Jean-Marie Lehn.

Véronique started her independent research career at the University of Oxford in 1998 in the the Department of Chemistry and was promoted to Professor of Chemistry in 2008. Since her appointment in Oxford, she has held a tutorial fellowship at Merton College Oxford, where she taught organic chemistry. Since 2022, she is the Waynflete Professor of Chemistry (Magdalen College). Her research aims at developing new approaches to address long-standing problems in the synthesis of fluorinated molecules including pharmaceutical drugs and probes for molecular imaging (Positron Emission Tomography), and a new programme on sustainability and circularity. She has coordinated European ITN projects and received funding from numerous bodies including two ERC Advanced Grants (2019–2024 and 2025–2029). She is the (co)author of >230 peer-reviewed publications and 10 patents.

Her research has been disseminated at numerous conferences and rewarded by multiple prizes and distinctions, including the 2015 ACS Award for Creative work in Fluorine Chemistry, the 2016 RSC Tilden Prize, the 2016 Tetrahedron Chair, the 2019 RSC Organic Stereochemistry Award, the 2019 Prelog Medal, the 2021 Henri Moissan Prize, the 2022 Arthur C. Cope Award, the 2022 EuChemS Female Organic Chemist of the Year Award, the 2024 Prous Institute - Overton and Meyer Award for New Technologies in Drug Discovery and the 2024 Davy Medal.

Véronique has also been elected Member of the European Academy of Sciences (EURASC) in 2017, Fellow of the Royal Society in 2019 and International Honorary Member of the American Academy of Arts and Sciences in 2022.

Dexi Weng

Dexyan Global, USA Comeall Technology, China

Dr.Dexi Weng earned a Ph.D. Degree from New York University in Polymer Science. He earned a bachelor degree from Harbin University of Science and Technology in Electronics Engineering. He earned an MBA degree from Northeastern University. He is one of the founders for Dexyan Global Poly Research Institute and All-Optical Network Global Consortium, all in USA and Comeall (Shanghai) Technology CO., Ltd.

He has been developing & promoting perfluorinated polymer based Gi-POF (graded index polymer optical fiber) technology for super-high speed data communications and all optical networks (AON). He proposed English words, FIBER, OPTICAL, and OPTICALize as verbs, & OPTICALization as noun derived thereof to conceptualize, lead and encourage the on-going paradigm shift from ELECTRONic to PHOTONic means/ways in data world in an effort to further improve performance in big-data world. OPTICALization is categorized into 5 phases which are concurrently being carried out all-over the world: 1) Data Transmission Media, 2) Data Ports, 3) Data Interconnects, 4) Data Processing/computing and 5) Data Visualization/Feedback. Chemistry plays a vital part in the data OPTICALization.

In this talk, Dr. WENG will present the concept of OPTICALization, technologies and Fluorine Chemistry's role therein, market prospects in USA and China.

Feng-Ling Qing

Shanghai Institute of Organic Chemistry, China

Feng-Ling Qing obtained his doctoral degree in 1990 from Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences. From 1992 to 1995, he worked as a postdoctoral researcher at Wyeth Research in the United States. In 1997, he was promoted to professor at SIOC of the Chinese Academy of Sciences. From 1999 to 2009, he served as the director of Key Laboratory of Organofluorine Chemistry at the Chinese Academy of Sciences. Since 2023, he has been serving as the director of the State Key Laboratory of Fluorine and Nitrogen Chemistry and Advanced Materials at SIOC, Chinese Academy of Sciences. From 2000 to 2022, he was a professor at Donghua University. He was selected as Cheung Kong Scholar Professor by the Ministry of Education of China in 2001, received the Distinguished Young Scholars Fund of National Natural Science Foundation of China in 2003, and was awarded the National Natural Science Award (2nd class) in 2019. His research focuses on organofluorine chemistry and fluorinated materials. Since starting independent research in 1995, he has published over 320 research papers.

Florian Kraus

Philipps-Universität Marburg, Germany

Florian Kraus studied chemistry at the universities of Regensburg, Germany, and San Diego, USA, and finished in 2003 with his diploma and in 2005 with his Ph.D. thesis. Starting his own research in the field of inorganic fluorine chemistry in 2006 at the Technische Universität München, he obtained the venia legendi in 2011. In 2014 he moved to Philipps-Universität Marburg as a Heisenberg full professor of inorganic chemistry.

Kraus focuses on inorganic solid-state fluorine chemistry and uranium chemistry. His current research interests are in basic science: chemistry of the highly reactive halogen fluorides XF3, and XF5 (X = Cl, Br); Mn(IV)-based fluoride phosphors such as K2SiF6:Mn; chemistry with fluorine plasma and the metal hexafluorides MF6; dry chemistry recycling of platinum and coinage metal compounds; chemistry of thorium and uranium; chemistry in water-like solvents such as NH3, BrF3, HCN, HF, and SO2.

He serves on the boards of the GDCh's Division of Solid-State Chemistry and Materials Research and the Fluorine Chemistry Working Group, is a DFG Review Board Member for Inorganic Solid State Chemistry and Materials Synthesis, and is a member of the DFG-Leopoldina Joint Committee on the Handling of Security-Related Research.

Petr Beier

Institute of Organic Chemistry and Biochemistry, Czech Republic

Senior group leader at IOCB Prague. He studied MSc at the University of Pardubice, Czech Republic, PhD at St. Andrews University, United Kingdom and postdoc at the University of Southern California, United States. Since 2007 he is a research group leader at the Institute of Organic Chemistry and Biochemistry, Academy of Science of the Czech Republic, Prague. He is a recipient of Alfred Bader Prize in organic chemistry (2013) and Royal Chemical Society Fluorine Prize (2017). His research interests are methodology development in organofluorine chemistry and the chemistry of main group elements, investigation of reactive intermediates (nitrenes, carbenes, carbanions, radicals) and reaction mechanisms.

PLENARY LECTURES

Intermolecular Recognition Phenomena Involving Poly-Fluoroalkyl Amphiphiles

*Pierangelo Metrangolo**

Laboratory of Supramolecular and Bio-Nanomaterials (SBNLab), Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milano, Italy.

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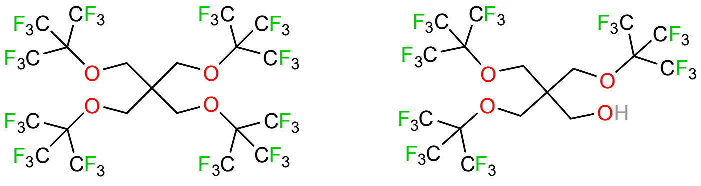
Due to the higher electronegativity and larger dimension of fluorine than hydrogen, perfluoroalkyl chains are bulkier than their hydrogenated counterparts, characterized by greater rigidity, and generally assume a helical conformation to minimize steric hindrance. All these properties induce in perfluorocarbons peculiar self-assembling properties, thus generating functional materials with improved physical properties. Unfortunately, linear-chain perfluorocarbons (PFCs) with more than four -CF_2- units show long-lasting persistence in the environment, high tendency to accumulate in humans and animals, and suspected toxicity. The use of short branched perfluorinated chains, as those present in perfluoro-*tert*-butoxyl-functionalized pentaerythritol derivatives [1], guarantee the insertion of a high number of equivalent fluorine atoms with an enhanced lability and biodegradability. As shown in Figure 1, these molecules bear a high number of equivalent ^{19}F atoms making them exceptional probes for ^{19}F-Magnetic Resonance Imaging (MRI) applications [2]. However, superfluorinated molecules are not directly dispersible in aqueous solutions, thus chemical functionalization with hydrophilic moieties or tailored formulations are needed for obtaining their dispersibility in this medium. For this purpose, we developed novel dendrimeric amphiphiles functionalized at their core with branched fluorinated chains, starting from the F27 derivative [3]. The interesting self-assembly properties of these new families of fluorinated dendritic amphiphiles will be discussed in detail [4].



PERFECTA **F_{27}**

Figure 1. Chemical structure of PERFECTA, which shows 36 magnetically equivalent fluorine atoms, and of its derivative tri-perfluoro-*tert*-butoxyl-functionalized pentaerythritol (F27). This molecule shows 27 equivalent fluorine atoms and a free hydroxyl group suitable for further functionalization.

References

[1] Chirizzi, C.; *et al. J. Am. Chem. Soc.*, **2021**, *143*, 12253-12260.
[2] Rosati, M.; *et al. Macromolecules*, **2022**, *55*, 2486-2496.
[3] Laurent, Q.; *et al. Angew. Chem. Int. Ed.*, **2025**, *64*, e202419996.
[4] Baldelli Bombelli, F.; Metrangolo, P.; Cavallo, G.; Bono, N.; Candiani, G.; Rosati, M.; Pinter Lauria, G.; Marcuzzo, S. *Non-Viral Vectors for Gene Therapy.* WO2023170543A1.

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NSF Engineering Research Center EARTH (Environmentally Applied Refrigerant Technology Hub)

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This presentation will provide an overview of a new U.S. National Science Foundation (NSF) Engineering Research Center (ERC) named EARTH (Environmentally Applied Refrigerant Technology Hub). Heating, ventilation, air conditioning, and refrigeration (HVACR) are essential to human quality of life but exact a significant environmental toll. Most current refrigerants are high-global-warming-potential (GWP) hydrofluorocarbons (HFCs) with up to 4000 times the impact of CO_2. High HVACR-associated energy consumption and HFC leaks account for 7.8% of total greenhouse gas emissions. HFCs' chemical stability, combined with challenges associated with separating HFC refrigerant blends into components, make sustainable recycling and repurposing of these refrigerants difficult. In addition, tightening U.S. regulations have created a market for illegal HFC imports. The American Innovation and Manufacturing (AIM) Act mandates an 85% phasedown of HFCs over the next two decades, but these challenges threaten that goal. Even if the technical goals are met, implementing such sweeping changes will require societal and industrial adoption and a greatly expanded U.S. HVACR workforce. ERC EARTH will use a team-science approach to bring together talent in engineering (chemical, environmental, mechanical, and materials), architecture, business, chemistry, economics, geography, history, law, psychology, and entrepreneurship in one Innovation Ecosystem to co-create convergent technical and societal solutions with industry partners, technical and community colleges, professional organizations, regulators, and end users. EARTH's vision is to create a transformative "sustainable refrigerant lifecycle" to address the HVACR ecosystem's key technical and societal challenges: (1) lowering HFC emissions, (2) creating safe, property-balanced replacement refrigerants, and (3) increasing HVACR energy efficiency. In addition, EARTH will work toward workforce goals co-created with industry to increase the number of HVACR engineering researchers and will involve community and technical colleges to address workforce gaps through coordinated outreach and training, with a focus on women, native people, and tribal nations.

With stakeholder input and integration across fundamental knowledge, enabling technologies, and system testbeds, EARTH will convergently address the societal problem of refrigerant environmental impacts. Refrigerant leaking and venting will be addressed by new separation, conversion, security-tagging, and waste-refrigerant-reuse technologies, spurring sustainable decision-making and new startups. Novel, safe, property-balanced, low-flammability and low environmental-impact refrigerants will be explored with molecular simulations of candidate fluids, development of solid-state materials, regulatory-impact economic analysis, and corporate-innovation insights. Higher HVACR energy efficiency will be obtainable through new energy-efficient dehumidification materials, refrigerant-specific leak sensors, alternative refrigeration cycles, systems modeling, lifecycle analysis, technoeconomic analysis, and exploration of corporate, environmental, social, and governance activities. Crosscut themes - Synthesis & Characterization, Behavior & Policy, and Modeling & Analysis - will integrate research with all ERC pillars. The EPA estimates the AIM Act's successful implementation from 2022 to 2050 will net benefits of $272 billion and emission reductions of 4.6 billion tons of CO_2. It will also create 150,000 new jobs, increase U.S. manufacturing by $39 billion, and prevent a 0.5 °C increase in global temperature. EARTH will enable and accelerate these benefits with new technologies, data-informed regulatory guidance, and industry and stakeholder buy-in. By addressing the technical, environmental, and societal challenges of replacing high-GWP refrigerants, EARTH's research will generate scientific knowledge, engineering products, environmental-policy recommendations, and industry and stakeholder behavioral changes to stimulate this HVACR-ecosystem transformation.

Rethinking Fluorine Chemistry with Global Challenges in Mind

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The Gouverneur laboratory has developed new approaches for the synthesis of fluorochemicals for applications in the life and material sciences. This work has enhanced our fundamental understanding of alkali metal fluoride reactivity, and led to the invention of hydrogen bonding phase transfer catalysis (HBPTC), a new concept in organocatalysis opening new opportunities in organic chemistry. In this lecture, the discussion will focus on innovative approaches aimed at addressing the challenges currently facing the fluorochemical industry. A specific highlight is the demonstration that it is possible to convert naturally occurring fluorspar (CaF_2) into complex fluorochemicals applying a method that bypasses the necessity to manufacture hydrofluoric acid, a toxic and highly dangerous acid. Another recent advance is the design of a method for the destruction of PFAS coupled with fluorine recovery in the spirit of a circular fluorine economy.

Calcium Fluoride (fluorspar) to Perfluoroorganic Materials to Data OPTICALization

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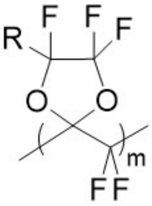
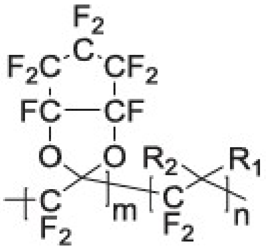
With calcium fluoride as the main component, fluorspar has been finding ever increased industrial uses in OPTICALization of data communications, especially in making graded-index polymer optical fibers / waveguides, photonic components [1]. As a starting material, fluorspar's commercial potential usage in OPTICALization is huge. The derived devices, especially the perfluorinated polymer optical fibers and waveguides, photonic devices will play very important roles in the process of OPTICALization of data communications. The increased applications of these materials open up more avenues for fluorspar industry & fluoro-chemistry [2,3]. With fluorine entity imparting temperature-resistance, fluid resistance among other beneficial properties, fluorine-containing molecules or polymers will make the end products for data communication exhibiting better properties than "regular" counterparts [3,4].
In this presentation, advances in synthesis of fluorine-containing polymers and polymer optical fibers made of will be presented. Properties of these original materials will be examined. Potential commercial applications in OPTICALization of super-big data communications will be discussed.





References

[1]. D. WENG, "OPTICALization, An Internal Standard", Comeall (Shanghai) Tech. Co., Ltd, v1, 2022
[2]. D. WENG, "FIBER, An Internal Standard", Zhejiang GiPOF Optronics Tech. Co., Ltd, 2021
[3]. Y. OKAMOTO, Q. Du, K.KOIKE, F. MIKEŠ, T.C.MERKEL, Z. HE, H. ZHANG and Y. KOIKE, "New amorphous perfluoro polymers: perfluorodioxolane polymers for use as plastic optical fibers and gas separation membranes", Polym. Adv. Technol. 2016, 27 33–41.
[4]. Y. KOIKE, "Fundamentals of Plastic Optical Fibers", p119-p137, (Wiley-VCH, 2015).

Synthesis and Application of Pentafluorosulfanyl (SF_5)-Containing Reagents

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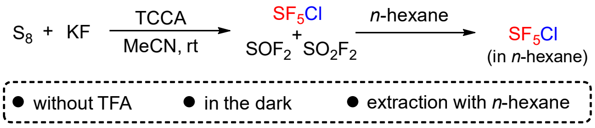
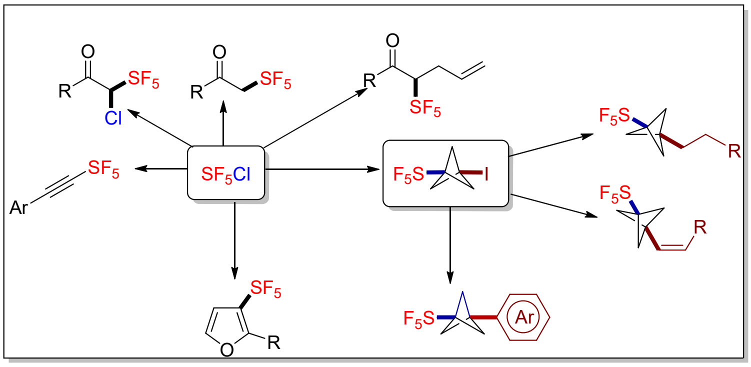
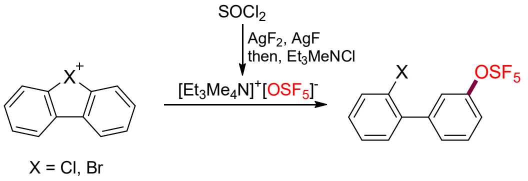
Recently under the Organization for Economic Co-operation and Development's broadened definition of per- and polyfluoroalkyl substances (PFAS), any substance that contains at least one fully fluorinated methyl (CF_3) or methylene (CF_2) without any H, Cl, Br, or I attached to it could be classified as a member of the PAFS family and subject to restriction. As a result, the 107 of 360 fluorinated small-molecule drugs including the anti-HIV medication Lenacapavir that fit with the new definition may be subject to future restrictions. According to this definition, pentafluorosulfanylated (SF_5) compounds are precluded from the scope of PFAS and thus considered as environmentally friendly fluorinated substances. However, the synthesis of pentafluorosulfanyl (SF_5)-containing compounds is less developed. At this meeting, new reactions of pentafluorosulfanyl chloride will be presented: 1) Pentafluorosulfanylation of diazo compounds and ethynylbenziodoxolone reagents with pentafluorosulfanyl chloride (SF_5Cl) that was prepared as the easy-to-handle solution in n-hexane under gas-reagent-free conditions. 2) Synthesis of 1-iodo-3-pentafluorosulfanylbicyclo[1,1,1]pentane (SF_5-BCP-I) from the reaction of pentafluorosulfanyl chloride, [1.1.1]propellane and CH_2I_2 and its reaction. In addition, a safe and efficient access to various pentafluoro(aryloxy)-λ^6-sulfanes ($ArOSF_5$) through the reaction of hypervalent λ^3-chlor(brom)anes with $[Et_3MeN]^+[OSF_5]^-$ will also be reported.







Oxidation of Halogen Pentafluorides - and N_2?

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Platinum hexafluoride is known for its enormous oxidizing power. It gained its popularity mainly due to its ability to oxidize Xe, forming the first noble gas compound "$XePtF_6$".[1] It was only a few years later that the actual composition of the reaction products could be determined, which was a mixture of $[XeF][PtF_6]$ and $[XeF][Pt_2F_{11}]$.[2] In addition to Xe, PtF_6 is also able to oxidize various other compounds whose oxidation seemed impossible at the time. For example, NF_3 or ClF_5 can be oxidized to the coordinatively saturated cations $[NF_4]^+$ or $[ClF_6]^+$.[3,4] However, the formation of $[BrF_6]^+$ by the reaction of BrF_5 and PtF_6 is not possible. To oxidize BrF_5, even stronger oxidizing agents such as $[KrF]^+$ or $[NiF_3]^+$ generated in situ are required.[5]
Our work shows that RuF_6 is able to oxidize all known halogen pentafluorides XF_5 (X = Cl, Br, I) at room temperature in aHF to the respective $[XF_6]^+$ salts, according to equation (1).

$$XF_5 + 2\,RuF_6 \longrightarrow [XF_6][Ru_2F_{11}] \qquad (1)$$

Surprisingly, if the reaction above is carried out under an atmosphere of N_2, the formation of the compound $[NF_4][Ru_2F_{11}]\cdot BrF_5$ is observed. The compounds obtained were characterized using various methods, e.g. Raman spectroscopy and single-crystal X-ray structure analysis. Figure 1 shows the crystal structure.

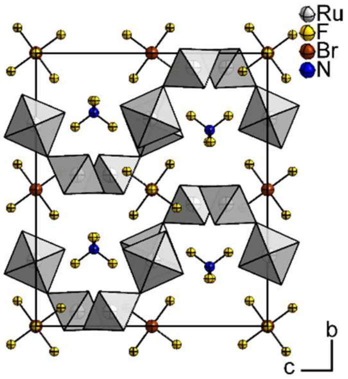

Figure 1. Figure caption: Calibri 11 pt, single line spacing.

References
[1] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218–218.
[2] L. Graham, O. Graudejus, N. K. Jha, N. Bartlett, *Coord. Chem. Rev.* **2000**, *197*, 321–334.
[3] K. O. Christe, W. W. Wilson, E. C. Curtis, *Inorg. Chem.* **1983**, *22*, 3056–3060.
[4] F. Q. Roberto, *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 737–740.
[5] T. Schroer, K. O. Christe, *Inorg. Chem.* **2001**, *40*, 2415–2419.

Fluorinated Organic Azides in Synthesis and Bioconjugation

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Organic azides are valuable intermediates in synthesis, bioconjugation, drug discovery, pharmacology, or in material science.[1,2] We introduced a new family of organic azides – α-fluorinated azidoalkanes and showed that they display a significantly increased stability than azidoalkanes and better reactivity in CuAAC reactions.[3,4] Photocatalytic denitrogenation of azidotrifluoromethane affords *N*-trifluoromethylaziridines via trifluoromethylnitrene.[5] *N*-Fluoroalkyl 1,2,3-triazoles prepared by the click reaction from fluorinated azides undergo various denitrogenation reactions: 1. Thermal denitrogenation to ketenimines and isoquinolines.[6] 2. Rh-catalyzed denitrogenation to *N*-(per)fluoroalkyl azoles.[7] 3. Acid-mediated denitrogenation via vinyl cations (Figure 1).[8]

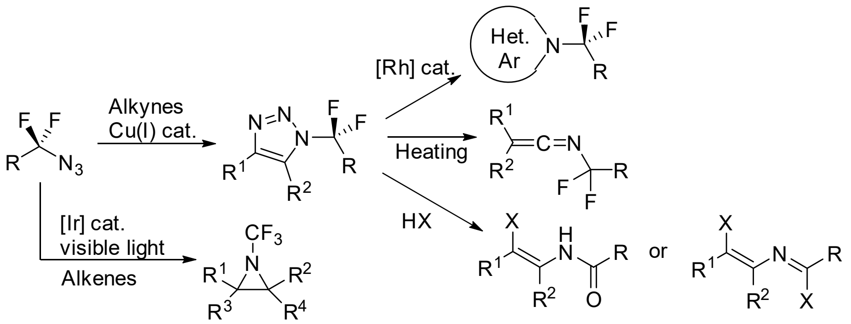

Figure 1. Selected reactivity of fluorinated azidoalkanes.

In this overview lecture, the important aspects of the generation, properties and reactivity of fluorinated azides will be summarized. This work was financially supported by the Czech Science Foundation (23-04659S) and the Czech Academy of Sciences (RVO: 61388963).

References

[1] Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V., *Angew. Chem., Int. Ed.* **2005**, *44*, 5188.
[2] Meldal, M.; Diness, F., *Trends Chem.* **2020**, *2*, 569.
[3] Blastik, Z. E.; Voltrová, S.; Beier, P., et al., *Angew. Chem., Ing. Ed.* **2017**, *56*, 346.
[4] Bakhanovich, O.; Beier, P., *Chem. Eur. J.* **2020**, *26*, 773.
[5] Baris, N.; Dračínský, M.; Tarábek, J.; Filgas, J.; Slavíček, P.; Ludvíková, L.; Boháčová, S.; Slanina, T.; Klepetářová, B.; Beier, P. *Angew. Chem., Int. Ed.* **2024**, *63*, e202315162.
[6] Kubíčková, A.; Markos, A.; Voltrová, S.; Marková, A.; Filgas, J.; Klepetářová, B.; Slavíček, P.; Beier, P., *Org. Chem. Front.,* **2023**, *10*, 3201.
[7] Motornov, V.; Markos, A.; Beier, P., *Chem. Commun.,* **2018**, *56*, 3258.
[8] Markos, A.; Janecký, L.; Chvojka, T.; Martinek, T.; Martinez-Seara, H.; Klepetářová, B.; Beier, P., *Adv. Synth. Catal.,* **2021**, *363*, 3258.

Keynote Speakers

Short Biography & Abstracts

Marie-Pierre Krafft

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Marie Pierre Krafft's research focusses on the design, engineering and investigation of fluorocarbon-promoted molecular self-assemblies, colloids and interfaces, including nanoemulsions, microbubbles, micelles and vesicles, life-mimicking active droplets, microfluidic droplets, and fluorocarbon-based therapeutics. She is also concerned with PFAS-related environmental remediation issues, including remediation of heavily polluted sites. She published over 200 papers, holds 12 patents, delivered over 100 invited lectures in International Meetings. She received Awards from the French Académie des Sciences, Chemical Society of Japan, Fluorous Technology Committee, is a Member of the European Academy of Sciences and Chevalier de la Légion d'honneur. She is Co-Editor-in-Chief of Current Opinion in Colloid and Interface Science and sits on the Editorial Board of Scientific Reports and of Frontiers in Soft Matter. She led several projects with potential benefits for the society in the medical field and in material science that were supported by the European Commission, National Agency for Research, CNRS-Innovation and by Industry (Areva, Superbranche, TotalEnergies).

Beate Koksch

Freie University of Berlin, Germany

Professor Beate Koksch received her diploma in Chemistry and PhD in Biochemistry from the University of Leipzig. She pursued her postdoc as a DFG research fellow in the laboratories of Professors M R Ghadiri and C F Barbas, III at The Scripps Research Institute, La Jolla, California. In 2000, she started her independent career under the mentorship of Professor Dr K Burger at the University of Leipzig. Since 2004, she is professor of organic and natural product chemistry at Freie Universität Berlin, Germany. Her group studies complex folding mechanisms that occur in neurodegenerative diseases, develops new multivalent scaffolds and investigates the impact of fluorine on amino acids, proteins and bacterial cells. For her contributions to fluorine chemistry at the interface of chemistry and biology as well as protein science and engineering she received the ACS Award for Creativity in Fluorine Chemistry 2021.

Matthew Hopkinson

Newcastle University, UK

Matthew Hopkinson studied chemistry at the University of Oxford (UK) and conducted doctoral studies under the supervision of Prof. Véronique Gouverneur on gold-catalysed coupling reactions and novel fluorination methodologies for Positron Emission Tomography (PET) imaging. During this time, he was funded by a CASE award from GlaxoSmithKline and at various times conducted research at their Clinical Imaging Centre (CIC) in London. For his postdoctoral studies, he moved to the group of Prof. Frank Glorius at the WWU Münster in Germany, where he was awarded a scholarship from the Alexander von Humboldt foundation. His research there focused on transition-metal and photocatalysis, specialising in methodology development using visible light as an energy source. In 2016, he started his independent career at the Freie Universität Berlin as a Junior Professor before moving back to the UK in 2021 to take up his current position as a Senior Lecturer in Organic Chemistry at Newcastle University. His group works on synthetic methodology development focusing on organofluorine chemistry, organocatalysis and photochemistry.

Berthold Hoge

Universität Bielefeld, Germany

Currently, Berthold Hoge holds the position of Professor (W2) at the University of Bielefeld. Prior to this role, he served as a Lecturer at the University of Cologne from 2004 to 2009 and as a Visiting Lecturer at the Technical University of Aachen between 2004 and 2005. He completed his habilitation at the Technical University of Aachen between 1998 and 2004, where he conducted research on "Strategies for the synthesis of chiral, bidentate bis(perfluoroorganyl)phosphane ligands" under the supervision of Prof. D. Naumann at the University of Cologne. Before that, he completed a Postdoctoral Fellowship at the University of Southern California, working on "Synthesis and properties of hypervalent halogen oxides and oxide fluorides" with Prof. K. O. Christe from 1997 to 1998.

He earned his PhD in 1997 at the University of Wuppertal, focusing on "Synthesis and properties of fluoroalkyl derivatives of cadmium, copper, and silver," under the guidance of Prof. R. Eujen. His academic foundation was laid during his Master's studies at the University of Wuppertal, where he researched the "Synthesis and NMR spectroscopic characterization of difluoromethyl derivatives of tin and cadmium" with Prof. R. Eujen, and during his undergraduate studies in Chemistry at the same institution from 1988 to 1994.

Cormac Murphy

University College Dublin, Irland

Cormac studied biochemistry at Queen's University Belfast (1994) followed by a PhD investigating biological fluorination and defluorination in Streptomyces cattleya (1998). After postdoctoral work in Dalhousie University, Canada and St Andrew's University, Scotland he was appointed as an assistant lecturer in the Department of Industrial Microbiology in University College Dublin. He is currently a professor in the UCD School of Biomolecular and Biomedical Science and is the Head of School. His research investigates biotransformation of fluorinated xenobiotic compounds such as PFAS in microorganisms, in particular the fungus Cunninghamella elegans.

Kazuhiko Matsumoto

Graduate School of Energy Science, Japan

He studied chemistry at Kyoto University where he received his PhD degree in 2004. He extended his research areas as a postdoc at Aichi Institute of Technology, McMaster University, and Kyoto University. He was appointed Assistant Professor in 2010 at Kyoto University and was promoted Associate Professor in 2015. His research interests are in inorganic fluorine chemistry and electrochemistry including structural characterization of new chemical species, synthesis and application of ionic liquids, and evaluation of electrolyte and electrode materials for electrochemical devices and processes.

KEYNOTE TALKS

Per- and Polyfluoroalkyl Substances (PFASs): A Tale of Two Faces Focusing on the Supramolecular Self-Assembling Propensity of PFAS Surfactants

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PFASs have become a global contamination concern. Since the 1940s, these exceptionally stable anthropogenic chemicals—both molecular and polymeric—have been widely used in industry and consumer products. Once released, they disperse through air and water, adhering to surfaces like rock, sediment, concrete, and tarmac. Nowadays, humans, animals, and plants face widespread exposure to air, dust, soil, food, and water. Some PFASs are now recognized as highly persistent, bioaccumulative, and toxic, and are now being strictly regulated [1]. The unique properties of PFASs, and particularly the strength of the C–F bond, stem from fluorine's distinctive position in the Periodic Table. Fluorinated surfactants exhibit the uttermost ability to form robust supramolecular self-assemblies (SS-A) in aqueous solutions and at various interfaces [2]. Our research focuses on investigating PFAS SS-As, including surface micelles, vesicles, fibers, ribbons, tubules, and further large complex microstructures (Fig. 1) at various environmentally relevant interfaces. We have developed methodologies for identifying, analyzing, and quantifying such supramolecular structures. Typically, we use spontaneously adsorbed (Gibbs) films or Langmuir monolayers to investigate the PFAS self-assemblies in their early stages of formation. Their morphology, structure, molecular orientation, and compositional analysis are studied using such advanced techniques as grazing-incidence X-ray scattering (GISAXS) [3], interfacial rheology [4], infrared reflection–absorption spectroscopy (IRRAS) [5], neutron reflectometry (NR) coupled with ellipsometry [6], Brewster angle microscopy (BAM), and atomic force microscopy (AFM) [7]. The self-assembling behavior of PFASs, which has until now been largely overlooked, is liable to significantly influence their environmental fate and impact remediation efforts [8].

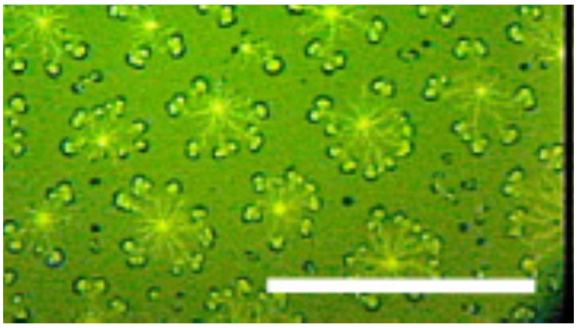

Figure 1. The formation of complex, flower-like structures reflects the impact of adding an (F-alky)alkane to a phospholipid monolayer, as observed by fluorescence microscopy. The bar represents 100 µm. From [7].

[1] M.P. Krafft, J.G. Riess, Chemosphere, **2015**, 129, 4-19; M.P. Krafft, J.G. Riess, Curr. Opin. Colloid Interface Sci., **2015**, 20, 192-212.
[2] M. Tanaka, M.P. Krafft, A. Pasc, NPG Asia Materials, **2023**, 15, 23; M.P. Krafft, Acc. Chem. Res., **2012**, 45, 514-524.
[3] W. Abuillan, M. Veschgini, S. Mielke, A. Yamamoto, X. Liu, O. Konovalov, M.P. Krafft, M. Tanaka, ChemPhysChem, **2019**, 20, 898-904.
[4] S. Mielke, W. Abuillan, M. Veschgini, X. Liu, O. Konovalov, M.P. Krafft, M. Tanaka, ChemPhysChem, **2019**, 20, 1698.
[5] C. Schwieger, X.-H. Liu, M.P. Krafft, Phys. Chem. Chem. Phys., **2017**, 19, 23809-23813.
[6] X. Liu, C. Counil, D. Shi, E.E. Mendoza-Ortega, A.V. Vela-Gonzalez, A. Maestro, R.A. Campbell, M.P. Krafft, J. Colloid Interface Sci., **2021**, 593, 1-10.
[7] H. Nakahara, M.P. Krafft, O. Shibata, ChemPhysChem, **2020**, 21, 1-6.
[8] M.P. Krafft, C. R. Acad. Sci., **2025**, in press.

Fluoropeptides as Biodegradable Biopolymers

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Fluorine as a substituent causes drastic changes in the biophysical properties of organic molecules and polymers. This results in highly appreciated properties of drugs and materials that are ubiquitous in our everyday lives today. However, the unique stability of the C-F bond can be problematic if this leads to poor biodegradability. Combining the special material properties of fluoropolymers with the biocompatibility of peptides could be an attractive solution.

The incorporation of fluorine substituents into otherwise hydrophobic amino acid side chains induces a polarity that no other functionality can generate in this form. This special polarity leads to drastic changes in the biophysical properties of peptides in terms of hydrophobicity, lipophilicity, solubility as well as folding and proteolytic stability; criteria that are of utmost importance for biomolecular recognition, self-assembly and, thus, the properties of peptide-based biomaterials. [1] Generally, the combination of fluorine substituents, which lead to the much-described and widely used omniphobic properties in organic polymers, with the water-soluble properties of peptides (depending on their sequence and folding) promises new classes of compounds with extremely interesting properties. Fluoropeptides, which consist exclusively or to a large extent of fluorinated amino acids, offer a wide range of unexplored possibilities in terms of folding, self-assembly and material properties. We have recently taken the first steps into this uncharted scientific territory. [2, 3]

The lecture will present the first polyfluorinated peptides that consist of more than 50 % of fluorinated amino acids. They represent an amphipathic peptide motif combining long stretches of fluorinated amino acids containing one to three fluorine substituents in the side chain of ethyl glycine with a short stretch of positively charged lysine residues that mediate solubility in aqueous medium. The structural and biomaterial properties of this new class of compounds are discussed here. This design is comparable to organic co-block polymers. The application of this class of fluoropeptide conjugates for the encapsulation of hydrophobic drugs and their specific delivery to their cellular targets is also presented. In addition, we are investigating how isolated enzymes and whole microorganisms are able to cleave C-F bonds of fluorinated peptides and amino acids. These results open up new avenues for the development of biomaterials containing fluorine.

References

[1] A.A. Berger, J.-S. Völler, N. Budisa, B. Koksch. *Acc. Chem. Res.* **2017**, 50 (9), 2093

[2] S. Chowdhary, R.F. Schmidt, A.K. Sahoo, T. tom Dieck, T. Hohmann, B. Schade, K. Brademann-Jock, A.F. Thünemann, R.R. Netz, M. Gradzielski, B. Koksch. *RSC Nanoscale* **2022**, 14, 10176

[3] T. Hohmann, S. Chowdhary, K. Ataka, J. Er, G. H. Dreyhsig, J. Heberle, B. Koksch. *Chem. Eur. J.* **2023**,e202203860

[4] M. F. Khan, S. Chowdhary, B. Koksch, C. D. Murphy. *Environmental Science & Technology* **2023***, 57*, 9762

Novel Methods for Installing Emerging Fluorinated Motifs

Matthew N. Hopkinson*

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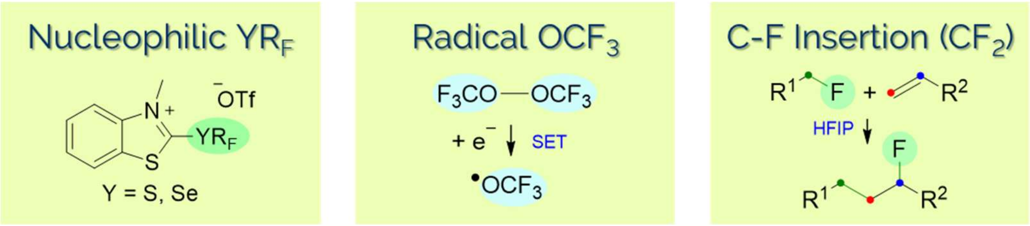
Fluorine incorporation can have a dramatic influence on the properties of functional organic molecules such as agrochemicals and pharmaceuticals. In addition to the more established single C–F fragments or CF_3 groups, recent years have seen a surge in interest in installing different types of fluorinated moiety that offer the potential for further enhancing compounds' biological or physical properties.[1] In our group, we have been interested in developing new synthetic approaches to such "emerging" fluorinated groups with a particular focus on fluoroalkyl chalcogenyl motifs such as the SCF_3 and OCF_3 moieties. For example, we have introduced a range of nucleophilic reagents that allow for the deoxygenative installation of SCF_3, $SeCF_3$ and related groups onto readily available alcohols and carboxylic acids.[2] Moreover, in a collaborative project with the Riedel group at the FU Berlin, we have developed radical methodologies towards aromatic, aliphatic and alkenyl (trifluoromethyl)ethers employing bis(trifluoromethyl)peroxide (BTMP) as an OCF_3 source.[3] In other project lines, we are interested in developing new methods for preparing compounds containing the *gem*-difluoromethyl motif, which is an important bioisostere of ether and carbonyl functions. Our approach make use of a little-explored concept in organofluorine chemistry: C–F insertion.[4] Whereas insertion into other C-halogen bonds is very well established, there are very few examples of insertion into C–F bonds, despite the inherent attractiveness of such processes in terms of atom economy and low waste production. Recently, we introduced an approach to C–F insertion that makes use of fluorine-specific hydrogen bonding interactions that allow for activation of benzyl and propargyl C–F bonds but do not lead to subsequent sequestration of the released fluoride.[5] In this talk, our recent results on these topics will be presented.



Scheme 1. Project lines in the Hopkinson group.

References

[1] Cahard, D.; Ma, J.-A. Emerging Fluorinated Motifs: Synthesis, Properties and Applications, Wiley-VCH, Weinheim, **2020**.
[2] Dix, S.; Jakob, M.; Hopkinson, M. N. *Chem. Eur. J.* **2019**, *25*, 7635.
[3] Maas, L. M.; Fasting, C.; Voßnacker, P.; Limberg, N.; Golz, P.; Müller, C.; Riedel, S.; Hopkinson,M. N. *Angew. Chem. Int. Ed.* **2024**, *63*, e202317770.
[4] Garg, A.; Haswell, A.; Hopkinson, M. N. *Chem. Eur. J.* **2024**, *30*, e202304229.
[5] Garg, A.; Gerwien, N. J.; Fasting, C.; Charlton, A.; Hopkinson, M. N. *Angew. Chem. Int. Ed.* **2023**, *62*, e202302860.

Perfluoroorganyl Gallium and Indium Chemistry: The First Main Group Element *Lewis* Acid Thionyl Chloride Adduct and its Chemistry

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Bielefeld University, Center for Molecular Materials, Univeristätsstraße 25, 33615 Bielefeld

**e-mail: b.hoge@uni-bielefeld.de*

In this talk we will summarize our results on the synthesis and properties of weakly coordinating tetrakis(perfluoroorganyl)gallates, $[Ga(R^f)_4]^-$, and -indates, $[In(R^f)_4]^-$ (R^f = perfluoroalkyl, -alkenyl and alkynyl). The application of the thermally and chemically robust $[Ga(C_2F_5)_4]^-$ salts in lithium-ion batteries is discussed. The *hard* and *soft Lewis* superacid tris(pentafluoroethyl)gallane as well as the *soft Lewis* superacid tris(pentafluoroethyl)indane were obtained as different *Lewis* base (D) adducts, $[M(C_2F_5)_3D]$ (M= Ga, In). Depending on the donor strength of the chosen Lewis base (D), the compounds exhibit regulated catalytic activities in hydrosilylations, chlorodefluorinations, *Friedel-Crafts* dimerizations and radical polymerizations. Catalytically very active adducts are accessible via dehydration of $[M(C_2F_5)_3(OH_2)_2]$ (M= Ga, In) with thionyl chloride. The very weakly bound thionyl chloride ligand of the resulting adducts $[M(C_2F_5)_3(SOCl_2)]$ can be selectively substituted by various other weak donor molecules such as florotrimethylsilane to yield the corresponding adducts $[M(C_2F_5)_3FSiMe_3]$.

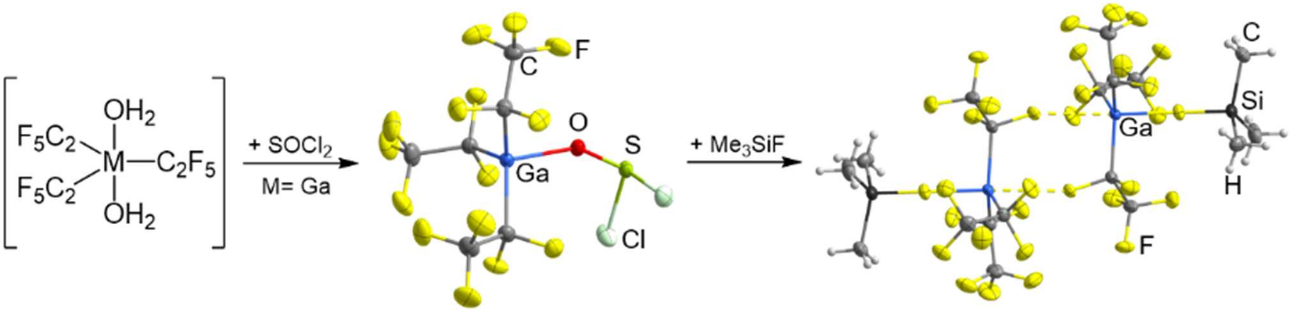

Figure 1. Synthesis and molecular structures of $[Ga(C_2F_5)_3(SOCl_2)]$ and $[Ga(C_2F_5)_3FSiMe_3]$.[1]

References

[1] Tölke, K.; Porath, S.; Neumann, B.; Stammler, H.-G.; Hoge, B. *Angew. Chem. Int. Ed.,* **2024**, e202408741.

Microbial Enzymes that Degrade PFAS

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(2) UCD Conway Institute, University College Dublin, Belfield, Dublin 4, Ireland

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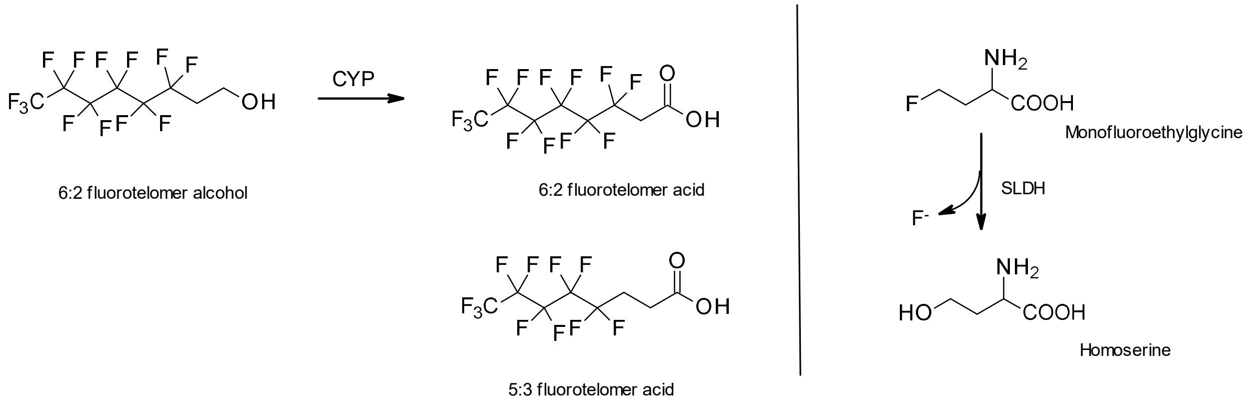
The application of per- and poly-fluorinated alkyl substances (PFAS) in numerous everyday products has resulted in widespread environmental contamination and potentially damaging impacts on human health. Although still commonly viewed as 'forever chemicals' because of their persistence in the environment, some microorganisms can degrade them, raising the possibility of bioremediation of PFAS contaminated waste streams. *Cunninghamella* fungi catabolise a range of PFAS yielding fluoride ion and smaller perfluorinated carboxylic acids [1]. Attention has now turned to uncovering the specific enzymatic steps that are responsible for the catabolism of these compounds, so that the limitations in biodegradation can be addressed. Previous inhibitor studies indicated that cytochromes P450 (CYPs) are involved in the process and some of the 32 CYPs of the fungus have now been expressed in the yeast *Pichia pastoris*. Whole cell biotransformation experiments in the transformed yeast have revealed the likely reactions that the CYPs are responsible for (Scheme 1). In parallel we have discovered a broad range hydrolase in a bacterium, *Serratia liquefaciens* [2], which can cleave carbon-fluorine bonds despite an active site composition that differs from known dehalogenases. The recent results investigating these enzymes will be presented.



Scheme 1. Fungal cytochromes P450 (CYP) and *S. liquefaciens* dehalogenase (SLDH) degrade C-F bonds

References
[1] Khan, M.F.; Murphy, C.D. *Environ. Sci. Pollut. Res.*, **2023**, *30*, 23613
[2] Khan, M.F.; Chowdhary, S.; Koksch, B.; Murphy, C.D. *Environ. Sci. Technol.*, **2023**, *57*, 9762

Fluorine Chemistry in Energy Applications

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Development of large-scale energy storage systems is an urgent challenge of our society, and there is a strong need for high-performance devices beyond the established secondary battery technology by considering the increasing energy demand and stable resource supply. Contribution of fluorine chemistry to energy storage systems is immeasurable, and it will be even more important in future. This talk overviews the role of fluorine chemistry in energy applications, including our previous and recent electrolyte works.

The PF_6^- salts are commonly utilized as electrolytes in lithium-ion batteries. Its high solubility, electrochemical stability, and Al passivation property, enable the design of high-performance cells working over long cycles. Although some fluorophosphate anions derived from PF_6^- were reported as effective additives for secondary batteries, details of their working mechanisms are not fully understood. The $PO_2F_2^-$ anion has a large dipole moment based on the two oxygen and two fluorine atoms (Figure 1). This well-known anion, which has been recognized for a long time, rose to an important counter-ion in electrolyte applications. In lithium ion batteries, addition of $Li[PO_2F_2]$ to the electrolyte is beneficial to improve battery performance. Our work identified $Na[PO_2F_2]$ also has similar effects in sodium secondary batteries through the formation of stable and ion-conductive layer on electrode surface. Combination of large organic cations, including alkylimidazolium and alkylpyrrolidinium, with $PO_2F_2^-$ provides a range of ionic liquids. In addition to the low viscosity and high ionic conductivity, the $PO_2F_2^-$-based ionic liquids exhibit a high donor property owing to the high polarity of this anion, which could affect the capacitance of double-layer capacitor. Incorporation of dicationic organic cations also enables the formation of dicationic ionic liquids based on $PO_2F_2^-$.

Introduction of oxalate ligand to the fluorophosphate and fluoroborate anions results in a series of fluorooxalatoanions ($PF_x(ox)_y$ and $BF_x(ox)_y$) (Figure 1 for $PF_4(ox)^-$ as an example). Such anions have different oxidative and reductive stabilities and work as surface-layer formers to the interface between the electrolyte and electrode in secondary batteries. Density functional theory calculations revealed the introduction of the oxalate ligand decrease the reductive stability of the anion, whereas partially substituted anion is the most unstable against oxidation.

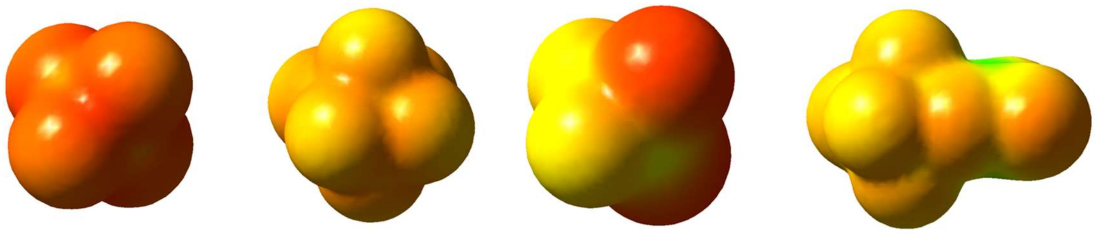

Figure 1 Electrostatic potential maps for BF_4^-, PF_6^-, $PO_2F_2^-$, and $PF_4(ox)^-$.

Scientific Programme: Talks

Sunday, August 3rd, 2025

Scientific Programme: Talks

Sunday, August 3rd, 2025

OPENING SESSION

Room: Auditorium II

16:30 – 18:30	**WELCOMING WORDS**

PLENARY SESSION - PIERANGELO METRANGOLO

Room: Auditorium II
Chair: Ana B. Pereiro and João M. M. Araújo, NOVA FCT, Portugal

17:15 – 18:15	**INTERMOLECULAR RECOGNITION PHENOMENA INVOLVING POLY-FLUOROALKYL AMPHIPHILES**
PL	**Pierangelo Metrangolo,** Politechnico di Milano, Italy

WELCOME RECEPTION

Room: Auditorium II

18:30 – 20:30	**FIRST FLOOR CCL – IN FRONT OF AUDITORIUM II**

Scientific Programme: Talks

Monday, August 4th, 2025

Monday, August 4th, 2025

PLENARY SESSION - MARK SHIFLETT

Room: Auditorium II
Chair: Bruno Ameduri, Institute Charles Gerhardt Montpellier, France

09:00 – 10:00	**NSF ENGINEERING RESEARCH CENTER EARTH (ENVIRONMENTALLY APPLIED REFRIGERANT TECHNOLOGY HUB)**
PL	**Mark B. Shiflett**, University of Kansas, USA

KEYNOTE SESSION - MARIE-PIERRE KRAFFT

Room: Auditorium II
Chair: Wojciech Grochala, University Warsaw, Poland

10:00 – 10:45	**PER- AND POLYFLUOROALKYL SUBSTANCES (PFASS): A TALE OF TWO FACES FOCUSING ON THE SUPRAMOLECULAR SELF-ASSEMBLING PROPENSITY OF PFAS SURFACTANTS**
KN	**Marie Pierre Krafft**, University of Strasbourg, France

PARALLEL SESSION I – ORGANIC CHEMISTRY

Room: Auditorium II
Chair: Dominique Cahard, CNRS, France

11:15 – 11:35	**THE SYNTHESIS AND PROPERTIES OF PARTIALLY FLUORINATED ALIPHATIC MOTIFS FOR APPLICATIONS IN MATERIALS AND PHARMACEUTICALS CHEMISTRY**
IL	**David O´Hagan**, University of St Andrews, UK
11:35 – 11:55	**REPURPOSING HFCS: A PATHWAY TOWARD GREENER FLUORINE CHEMISTRY**
IL	**Norio Shibata**, Nagoya Institute of Technology, Japan
11:55 – 12:10	**DIVERGENT ACCESS TO SULFUR FLUORINE GROUP-CONTAINING MOLECULES**
Oral	**Tim Gatzenmeier**, University of Nebraska-Lincoln, USA
12:10 – 12:25	**SELECTFLUOR PROMOTED DIRECTING GROUP AND TRANSITION METAL CATALYST FREE SITE-SELECTIVE C7 FLUORINATION OF 2-OXINDOLES**
Oral	**Madan Kumar,** Indian Institute Of Technology–Ropar (IIT–Ropar), India
12:25 – 12:40	**NEW FLUORINE-CONTAINING PROLINES FOR DRUG DISCOVERY**
Oral	**Ivan Kondratov**, Enamine Germany, Germany
12:40 – 12:55	**RADICAL PHOTOCHEMICAL DIFLUOROSULFOXIMINATION OF ALKENES AND PROPELLANES**
Oral	**Julien Paut**, University of Paris-Saclay, France
12:55 – 13:10	**RATIONAL DESIGN OF POLYFLUORINATED PEPTIDE-BASED BIOMATERIALS**
Oral	**Maurizio Iannuzzi,** Freie Universität Berlin, Germany

13:10 – 13:25	**TOWARDS A NEW DIRECT METHOD FOR THE SYNTHESIS OF ARYL DIFLUOROALKYL ETHERS FROM THE DIFLUOROMETHOXY $(-OCHF_2)$ MOIETY**
Oral	**Guillaume Siegel**, CNRS - Université de Strasbourg, France

PARALLEL SESSION I – INORGANIC CHEMISTRY & COMPUTATIONAL CHEMISTRY

Room: 3A
Chair: Beate Koksch, Freie University of Berlin, Germany

11:15 – 11:35	**CHEMISTRY OF MOF_5 AND $MOOF_3$**
IL	**Michael Gerken**, University of Lethbridge, Canada
11:35 – 11:55	**METAL FLUORIDE COMPLEXES AS FUNCTIONAL, STRUCTURE-DIRECTING BUILDING BLOCKS IN MOLECULAR MAGNETISM AND BEYOND**
IL	**Jesper Bendix**, University of Copenhagen, Denmark
11:55 – 12:10	**PHYSICOCHEMICAL PARAMETERS OF CHEMICAL CAPACITORS FEATURING FLUORINE-RICH OXIDIZERS AND SEPARATORS**
Oral	**Łukasz Wolański**, University of Warsaw, Poland
12:10 – 12:25	**NOVEL X_E–N AND X_E–O BONDED CATIONS: FORMATION, STRUCTURE, AND REACTIVITY**
Oral	**Kristian Radan**, Jozef Stefan Institute, Slovenia
12:25 – 12:40	**FROM COPPER TO LANTHANIDES: UNIQUE COMPLEXES WITH WEAKLY BOUND LIGANDS AND STABILIZED BY WEAKLY COORDINATING ANIONS**
Oral	**Przemysław J. Malinowski**, Centre of New Technologies, University of Warsaw, Poland
12:40 – 12:55	**DECODING THE FLUOROUS EFFECT WITH IR SPECTROSCOPY**
Oral	**Ruben Cruz**, Freie Universität Berlin, Germany
12:55 – 13:10	**SUPERCONDUCTIVITY IN LITHIUM HYDRIDE LAYER ENHANCED BY FLUORIDE SUBSTRATES**
Oral	**Piotr Szkudlarek**, University of Warsaw, Poland

PARALLEL SESSION I – CONTAMINANTS OF EMERGING CONCERN SPONSORED BY MAR2PROTECT

Room: 3B
Chair: Manuel M. Piñeiro, Universidade de Vigo, Spain

11:15 – 11:30	**IMPLEMENTING LIVINGLABS FOR GROUNDWATER PROTECTION: MAR2PROTECT EXPERIENCES IN EUROPE AND AFRICA**
IL	**Uta Wehn**, IHE Delft Institute for Water Education, The Netherlands
11:30 – 11:45	**NATURAL WETLANDS AS NATURE-BASED SOLUTIONS TO REMOVE POLLUTANTS AND PROMOTE THE GOOD QUALITY OF ESTUARINE SURFACE WATER**
IL	**C. Marisa R. Almeida**, CIIMAR, Porto University, Portugal
11:45 – 12:00	**REAL-TIME BIOMONITORING OF EMERGING CONTAMINANTS IN WATER RESOURCES**
IL	**Gideon Wolfaardt**, Stellenbosch University, South Africa

12:00 – 12:15	**INTEGRATED FIXED-BED COLUMN ADSORPTION AND SOLID-STATE FERMENTATION FOR EFFECTIVE REMOVAL OF BISPHENOL A USING BIOCHAR-BASED BIOMATERIALS**
IL	**Atef Jaouani**, University of Tunis El Manar, Tunisia
12:15 – 12:30	**NOVEL BIO-BASED ADSORBENTS FOR PFAS REMOVAL: A LIFE CYCLE ASSESSMENT APPROACH**
IL	**Jolanta Dvarionienė**, Kaunas University of Technology, Lithuania
12:30 – 12:45	**CHARACTERIZING AND ASSESSING REMOVAL PERFORMANCE OF TARGET NATURAL CONTAMINANTS IN A LAKE-WATER PILOT INSTALLATION IN THE NETHERLANDS**
IL	**Sergio Salinas**, IHE Delft, The Netherlands
12:45 – 12:55	**REMOVAL OF PER- AND POLY-FLUOROALKYL SUBSTANCES (PFAS) AND PHARMACEUTICALS ONTO ACTIVATED CARBON FROM WASTEWATER EFFLUENTS**
Oral	**María C. Naranjo**, Nova School of Science of Technology, FCT NOVA, Portugal
12:55 – 13:05	**SUITABILITY AND FEASIBILITY MAPPING TO ASSESS MANAGED AQUIFER RECHARGE SOLUTIONS TO COPE WITH GROUNDWATER POLLUTION**
Oral	**Isabel Gamallo Paz**, CETAQUA - Water Technology Center, Spain
13:05 – 13:15	**PHARMACEUTICAL REMOVAL FROM WASTEWATER BY ADSORPTION ON COMMERCIAL MATERIALS AND MOLECULARLY IMPRINTED POLYMERS**
Oral	**Elisa Girometti**, University of Bologna, Italy
13:15 – 13:25	**PFAS OPTICAL DETECTION APPROACH IN MAR2PROTECT**
Oral	**Moisés Barata**, Instituto de Telecomunicações, Portugal

PARALLEL SESSION II – INORGANIC CHEMISTRY

Room: Auditorium II
Chair: Florian Kraus, Philipps-Universität Marburg, Germany

14:30 – 14:50	**A POTPOURRI OF MAIN-GROUP FLUORINE CHEMISTRY**
IL	**Joseph S. Thrasher**, Clemson University, USA
14:50 – 15:05	**INVESTIGATION ON THE PENTAFLUOROOXOSULFATE (-OSF5) GROUP FOR INORGANIC AND (BIO)ORGANIC APPLICATIONS**
Oral	**Alexandre Millanvois**, Freie Universität Berlin, Germany
15:05 – 15:20	**SOLUBILITY INVESTIGATION OF SELECTED RE_2O_3 IN $(L_IF\text{-}N_AF)_{EUT}$ VS $(L_IF\text{-}N_AF\text{-}REF_3)$ MOLTEN SYSTEMS**
Oral	**Blanka Kubíková**, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia
15:20 – 15:35	**NEW BORYL AND DIBORATE DIANIONS**
Oral	**Merlin Bohn**, Universität Würzburg, Germany
15:35 – 15:50	**CRYSTAL STRUCTURE ELUCIDATION OF XENON COMPOUNDS BY 3D ELECTRON DIFFRACTION ON NANOMETER-SIZED CRYSTALLITES**
Oral	**Matic Lozinsek**, Jozef Stefan Institute, Slovenia
15:50 – 16:05	**ORGANYLPENTAFLUOROPHOSPHATE IONS**
Oral	**Jan-Hendrik Schröder**, Bielefeld University, Germany
16:05 – 16:20	**AUTOCATALYTIC DEGRADATION OF THE EXTREMELY POTENT GREENHOUSE GAS SF_6 IN BASIC ALCOHOLIC SOLUTION**

Oral	**Alexander Sietmann**, University of Innsbruck, Austria
16:20 – 16:35	**COPPER(I) COMPLEXES WITH WEAKLY BASIC LIGANDS: EXPLORING CU(I) INTERACTIONS WITH DINITROGEN AND FLUORINATED ARENES**
Oral	**Julie Willrett**, University of Freiburg, Germany

PARALLEL SESSION II – ORGANOMETALLIC CHEMISTRY

Room: 3A
Chair: Jean-François Paquin, Université Laval, Canada

14:30 – 14:50	**PREPARATION AND STUDIES OF FLUORINATED LIGANDS AND THEIR METAL COMPLEXES (PT, PD, ZN, ETC.): FROM CATALYSIS TO THE NON-COVALENT BOND-INDUCED C-H AND C-C BOND CHANGES**
IL	**Norman Lu**, Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taiwan
14:50 – 15:10	**NOVEL $CU^{III}CF_3$ COMPOUNDS RELEVANT TO C—C AND C—HETEROATOM BOND FORMATION**
IL	**Noel Nebra**, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA), CNRS - Université Toulouse III, France
15:10 – 15:30	**USING ORTHOCARBORANE AS A REPLACEMENT FOR THE ARYL GROUP TO GREATLY INCREASE THE OXIDIZING POWER OF "A_RIF_2" AND "$A_RI(OT_F)_2$"**
IL	**Jason L. Dutton**, La Trobe University, Australia
15:30 – 15:45	**ENHANCING PD(IV) STABILITY: TRIFLUOROMETHYL ORGANOPALLADIUM COMPLEXES**
Oral	**Juan Pueyo**, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Spain
15:45 – 16:00	**INVESTIGATION OF CAAC STABILIZED NIOBIUM AND TANTALUM PENTAFLUORIDES**
Oral	**Evelin Gruden**, Jožef Stefan Institute, Slovenia
16:00 – 16:15	**HOMOLEPTIC PLATINUM(IV)−CF3 AND $-OT_EF_5$ COMPLEXES AS POTENTIAL PRECURSORS FOR PLATINUM SPECIES IN HIGHER OXIDATION STATES**
Oral	**Niklas Limberg**, Freie Universität Berlin, Germany

PARALLEL SESSION II – CONTAMINANTS OF EMERGING CONCERN & FLUOROUS TECHNOLOGY SPONSORED BY LIFE4F-GASES

Room: 3B
Chair: Mark Shiflett, Wonderful Institute for Sustainable Engineering, University of Kansas, USA

14:30 – 15:00	**DEVELOPMENT AND SCALE-UP OF THIN FILM POLYMER MEMBRANES FOR THE SEPARATION AND RECYCLING OF FLUORINATED REFRIGERANTS**
IL	**Gabriel Zarca**, Universidad de Cantabria, Spain
15:00 – 15:15	**CAPTURE AND SEPARATION OF FLUORINATED GASES WITH HIGH GLOBAL WARMING POTENTIAL**
Oral	**Julio E. Sosa**, NOVA University Lisbon, Portugal
15:15 – 15:30	**AN INNOVATIVE HYBRID MEMBRANE-ADSORPTION (HAMSYS) TECHNOLOGY FOR THE SELECTIVE RECOVERY OF F-GASES FROM DEPLETED REFRIGERANT BLENDS**
Oral	**Javier Pinedo Alonso**, Apria, Spain
15:30 – 15:45	**LIFE-4-FGASES: DISSEMINATION AND COMMUNICATION ACTIVITIES**
Oral	**Rosa Monforte**, ERP, Portugal
15:45 – 16:00	**AN INNOVATIVE TECHNOLOGY FOR THE SELECTIVE RECOVERY OF F-GASES FROM DEPLETED REFRIGERANT BLENDS**
Oral	**Vanessa Gouveia**, Ambigroup, Portugal

PARALLEL SESSION III – ORGANIC CHEMISTRY

Room: Auditorium II
Chair: David O'Hagan, University of St Andrews, UK

17:00 – 17:20	**EXPANDING SF_5 CHEMISTRY**
IL	**Dominique Cahard**, CNRS, France
17:20 – 17:40	**COLLECTION OF QUALITY-EVALUATED PKA VALUES IN POLAR APROTIC SOLVENTS**
IL	**Ivo Leito**, University of Tartu, Estonia
17:40 – 17:55	**LIQUID-CRYSTALLINE PROPERTIES INDUCED BY INCORPORATING FLUORINES INTO D-Π-A TOLANE CONTAINING DECYLENEOXY CHAINS TERMINATED WITH IMIDAZOLIUM SALTS**
Oral	**Shigeyuki Yamada**, Kyoto Institute of Technology, Japan
17:55 – 18:10	**SIMPLE AND EFFICIENT APPROACH TO SULFONYL FLUORIDES**
Oral	**Masaaki Omote**, Setsunan University, Japan

PARALLEL SESSION III – MATERIALS & FLUOROUS TECHNOLOGY

Room: 3A
Chair: Jean-Marc Vincent, University of Bordeaux - CNRS, France

17:00 – 17:20	**KEY ASPECTS IN CORROSION OF SUPERALLOYS IN MOLTEN FLUORIDE SALTS**
IL	**Miroslav Boča**, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia
17:20 – 17:40	**LOW-ENERGY ELECTRON INTERACTIONS WITH F-GASES REFRIGERANTS**
IL	**Filipe Ferreira da Silva**, Universidade NOVA de Lisboa, Portugal
17:40 – 17:55	**CONTROLLED SYNTHESIS AND PROPERTIES OF POLYVINYLIDENE FLUORIDE BASED METAL-FLUORIDE SURFACE TREATMENTS FOR HIGH-NICKEL NCM CATHODES**
Oral	**Chunjoong Kim**, Chungnam National University, Korea
17:55 – 18:10	**NEW FLUORINATION METHODS OF MOLYBDENUM DISULFIDE (MOS$_2$) FOR ENHANCED H$_2$ PRODUCTION PERFORMANCES**
Oral	**Pierre Bonnet**, Université Clermont Auvergne, France
18:10 – 18:25	**FLUORINATED SOFT-MATTER – COMPARTMENTALIZED MICELLES, HEMIMICELLES, MESOPHASES, MICROEMULSIONS AND MORE**
Oral	**Eduardo J. M. Filipe**, Universidade de Lisboa, Portugal

PARALLEL SESSION III – CONTAMINANTS OF EMERGING CONCERN SPONSORED BY ALERT-PFAS

Room: 3B
Chair: Gabriel Zarca, Universidad de Cantabria, Spain

17:00 – 17:20	**FUNCTIONAL MATERIAL FOR PFAS REMOVAL**
IL	**Mona Semsarilar**, CNRS-European Institute of Membranes (IEM), France
17:20 – 17:40	**HOW CAN PFAS BE PHOTOCHEMICALLY ELIMINATED FROM AQUATIC COMPARTMENTS?**
IL	**Gilles Mailhot**, Institut de Chimie de Clermont-Ferrand, CNRS/Université Clermont Auvergne, France
17:40 – 18:00	**FLUORINATED METHANE DERIVATIVES HYDRATES: A MOLECULAR SIMULATION STUDY**
IL	**Manuel M. Piñeiro**, Universidade de Vigo, Spain
18:00 – 18:10	**ALERT-PFAS SOLUTIONS - DIGITAL TOOL FOR MODELLING PFAS RISK IN NATURAL ENVIRONMENTS**
Oral	**Albert Serra Compte**, Cetaqua, Spain
18:10 – 18:20	**MONITORING OF PFAS HOTSPOTS AND SURFACE WATER TREATMENT SOLUTIONS IN NATURAL AREAS**
Oral	**Joana C. Bastos**, NOVA University Lisbon, Portugal
18:20 – 18:30	**TRANSNATIONAL STRATEGY FOR THE DETECTION OF PFAS UNDER ALERT-PFAS PROJECT**
Oral	**Catarina Novo**, Instituto de Telecomunicações, Portugal

PARALLEL SESSION I

Organic Chemistry

The Synthesis and Properties of Partially Fluorinated Aliphatic Motifs for Applications in Materials and Pharmaceutical Chemistry

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The lecture will outline some of the research activity of our lab in St Andrews describing the preparation and properties of selectively fluorinated alkanes generated by linking fluoromethylene (-CHF-) groups in chains and rings. The flagship molecule, all-*cis*-1,2,3,4,5,6-hexafluorocyclohexane, is a highly polarised aliphatic ring, with very different properties to hydrocarbons and perfluorocarbons. The polarity arises because there are three co-aligned triaxial C-F bonds and the six fluorines occupy one face of the ring. Conversely the electropositive hydrogens occupy the other face. The fluorines polarise the rings increasing electrostatic attractions and lowering Log P's and these features emerge as an attractive property for applications in organic materials and medicinal chemistry.

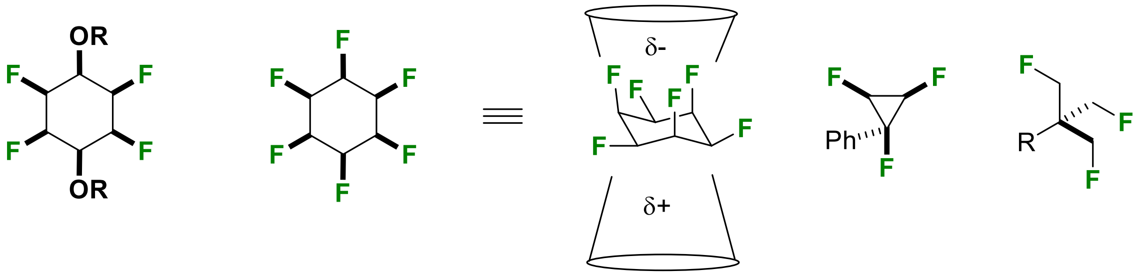

Figure 1. Selectively fluorinated aliphatic motifs

References

[1] T J Poskin, B. A. Piscelli, A. P. McKay, D. B. Cordes, Y. Eguchi, S. Yamada, R. A. Cormanich, D. O'Hagan *J. Org. Chem.*, **2024**, *89*, 18445 - 18451.

[2] M. He, B. A. Piscelli, R. A. Cormanich, D. O'Hagan, *J. Org Chem.*, **2024**, *89*, 4009–4018.

[3] A. Tarui, B. A Piscelli, N. Al-Maharik, J. M. Stewart, P. Niemcová, D. B. Cordes, A. P. McKay, C. D. Murphy, R. A. Cormanich, D. O'Hagan, *Chem Eur. J.*, **2024**, *30*, e202402532.

Repurposing HFCs: A Pathway Toward Greener Fluorine Chemistry

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The search for environmentally acceptable alternatives to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) prompted the widespread adoption of hydrofluorocarbons (HFCs) due to their negligible ozone depletion potential (ODP). Initially regarded as optimal substitutes, compounds such as trifluoromethane (HFC-23, CF_3H) and pentafluoroethane (HFC-125, CF_3CF_2H) quickly became prevalent, particularly as fire suppression agents and refrigerants in blends like R-503 and HFC-410A. Despite their advantages concerning ozone preservation, subsequent research and climate assessments revealed severe drawbacks associated with HFCs, primarily stemming from their substantial global warming potentials (GWPs)—notably, HFC-23 exhibits a GWP of 14,800, and HFC-125 a GWP of 3,450, making them potent greenhouse gases.

In response to this escalating climate threat, international policy frameworks such as the 2016 Kigali Amendment to the Montreal Protocol mandated progressive reductions in HFC production and usage, intensifying the urgency to develop innovative, efficient, and scalable methods for their neutralization or repurposing. Addressing this significant environmental challenge, our research group has dedicated efforts since 2012[1] to devising novel approaches to transform these problematic fluorinated gases into valuable chemical feedstocks. This strategy not only mitigates their environmental impact but also contributes positively to a sustainable circular economy within fluorine chemistry.

In this presentation, we will discuss recent progress in repurposing HFC-23 and HFC-125, highlighting synthetic routes to valuable fluorinated intermediates, and potential industrial implications.[2] Our results demonstrate how strategic chemical transformations can shift the perception of HFCs from environmental liabilities to resourceful chemical building blocks, setting a precedent for future developments in greener fluorine chemistry.

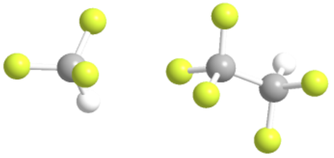

Figure 1. Trifluoromethane (HFC-23, CF_3H) (left) and pentafluoroethane (HFC-125, CF_3CF_2H) (right).

References
[1] N. Shibata and K. Kagawa, JP2012-242361 (JP2014091691).
[2] Y. Sumii and N. Shibata, *Chem. Rec.* **2023**, *23*, e202300117.

Divergent Access to Sulfur Fluorine Group-Containing Molecules

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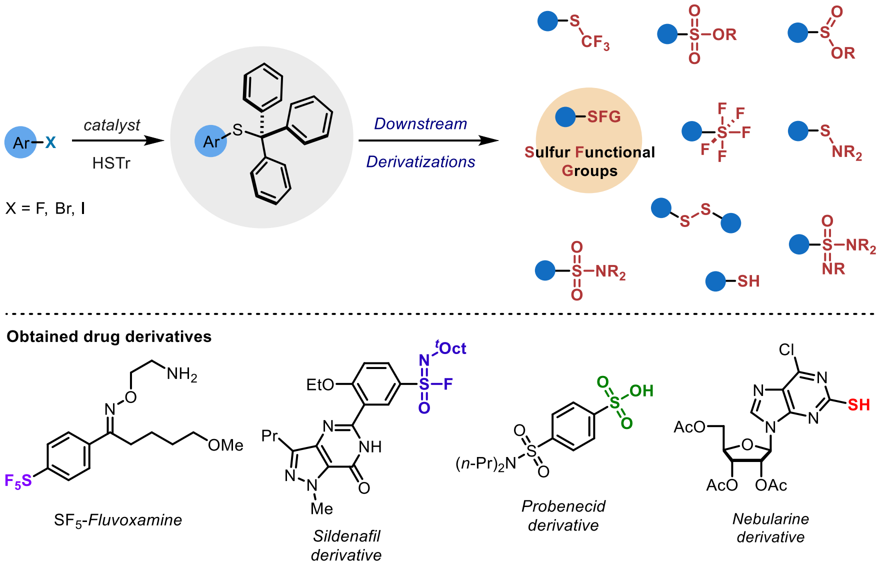
Sulfur-containing functional groups (SFGs) are increasingly important for modern medicinal chemistry and their large structural diversity provides many opportunities for lead optimization. In an effort to simplify the access of the full set of SFGs, we developed a versatile strategy utilizing (hetero)aryl trityl sulfides ($ArSCPh_3$) as the common precursors.[1] A mild and high yielding Pd-catalyzed thiotritylation cross-coupling methodology affords $ArSCPh_3$ compounds from (hetero)aryl bromides and iodides. Efficient chemoselective derivatizations provided access to eight different SFGs and SuFEx hubs, which open up further downstream derivatizations towards the full set of SFGs. Thereby obtainable sulfur motifs include aryl sulfur pentafluorides ($ArSF_5$), aryl tetrafluoro-λ^6-sulfanyl chlorides ($ArSF_4Cl$), aryl sulfonimidoyl fluorides (ArS(O)(NR)F), aryl sulfonyl fluorides ($ArSO_2F$), aryl sulfonic acids ($ArSO_3H$), and aryl sulfinyl fluorides (ArSOF), which are all valuable functional groups in modern drug discovery.

In particular, the introduction of pentafluorosulfanyl groups (SF_5) as an emerging modification to obtain enhanced molecular characteristics,[2] was achieved via the discovery of a direct pentafluorosulfanylation of thiolated arenes. The combination of onium halides with silver(II) fluoride (AgF_2) provided drastically enhanced oxidative fluorination conditions that enabled the single-step conversion of various thiophenol derivatives to SF_5-compounds in high yields and broad scope. The high reaction rate is accounted to an onium fluoroargentate(III)-mediated fluorine-atom transfer mechanism.



Scheme 1. Divergent access of a sulfur functional groups from thiotritylethers.

References

[1] L. Yue, T. Okazoe T. Gatzenmeier, K. Nozaki ChemistryEurope 2024, 2, e202400053.
[2] M. F. Sowaileh, R. A. Hazlitt, D. A. Colby ChemMedChem 2017, 12, 1481.

Selectfluor Promoted Directing Group and Transition Metal Catalyst Free Site-Selective C7 Fluorination of 2-Oxindoles

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Fluorine containing 2-oxindoles has garnered considerable attention over the past few decades, prompting extensive efforts toward their synthesis.[1] Despite the diverse fluorination strategies, the successful inclusion of a fluorine atom into an oxindole moiety in a site-selective manner other than C3 position remains a considerable challenge.

Thus, an efficient and operationally simple site-selective protocol for synthesizing fluorinated 2-oxindoles mediated by selectfluor has been developed under metal- and additive-free conditions. The C7 fluorinated 2-oxindole analogs were obtained in good to excellent yields without a directing group present at the N-centre of 2-oxindoles. Additionally, DFT analysis was performed using Gaussian 16 suite of programs to explain C5 vs C7 regioselectivity. Furthermore, post functionalization of fluorinated oxindoles at N-, O-, C3, and C5-centres and a step economical pathway for synthesizing WAY-255348 (drug molecule) have been achieved (Figure 1).[2]

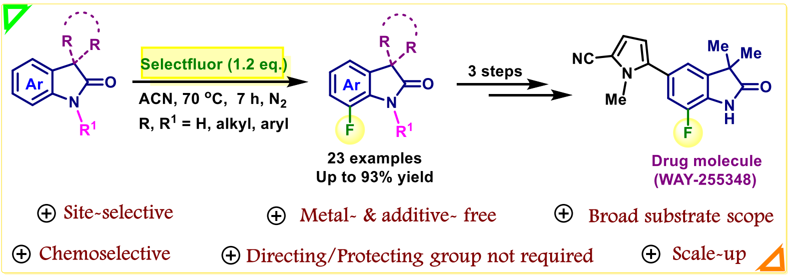

Figure 1. Site-selective fluorination of 2-oxindole and its application for the synthesis of WAY-255348.

References

[1] Hewawasam, P.; Gribkoff, V. K.; Pendri, Y.; Dworetzky, S. I.; Meanwell, N. A.; Martinez, E.; Boissard, C. G.; Post-Munson, D. J.; Trojnacki, J. T.; Yeleswaram, K.; Pajor, L. M.; Knipe, J.; Gao, Q.; Perrone, R.; Starrett, J. E. *Bioorg. Med. Chem. Lett.*, **2002**, *12 (7)*, 1023–1026; (b) Yin, X.; Wang, X.; Song, L.; Zhang, J.; Wang X. *Molecules* 2024*,* **29**, 3677; (c) Hamashima, Y.; Suzuki, T.; Takano H.; Shimura, Y.; Sodeoka, M. *J. Am. Chem. Soc.*, **2005**, *127 (29)*, 10164–10165.

[2] Lamba, M.; Kumar, M.; Mane, M. V.; Goswami, A. *Manuscript submitted*.

New Fluorine-Containing Prolines For Drug Discovery

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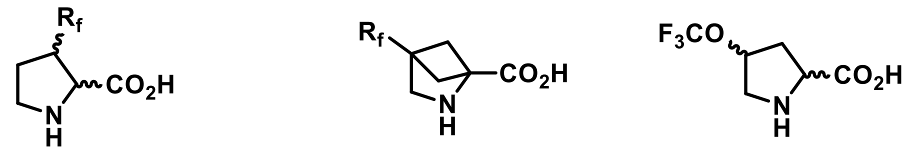
Proline is one of the most important natural aminoacids and its fluorinated analogs are important and valuable compounds for the research in peptide studies, protein engineering, medicinal chemistry and drug discovery [1,2]. Fluorinated motifs provide unique modulation capabilities and affect proline's acidity/basicity, lipophilicity, conformation, and trans/cis rotameric preferences of its amide derivatives. Therefore, medicinal chemists often apply fluorinated proline derivatives to improve the physicochemical properties, selectivity, and potency of novel pharmaceuticals.

During last decades a number synthetic approaches towards different fluorinated prolines were investigated [2]. Recently we developed synthetic approaches to several new aminoacids including stereoisomerically pure *cis-/trans-* 3-CF_3-and 3-C_2F_5-prolines **1,2** [3,4], CHF_2-/CF_3- methanoprolines **3,4** [5] and all isomers of 4-CF_3O-prolines **5** [6], filling the "gaps" in the space of fluorine containing prolines.

The particularities of synthetic approach as well structural and physical chemical properties of the synthesized amino acids and their derivatives will be discussed during the presentation.



$R_f = CF_3$ (**1**), C_2F_5 (**2**) $R_f = CF_3$ (**3**), CHF_2 (**4**) **5**

Figure 1. Fluorine-containing prolines **1-5**

References

[1] S. J. M. Verhoork *et al Biochemistry*, **2018**, *57*, 6132–6143.
[2] P. K. Mykhailiuk, *J. Org. Chem.*, **2022**, 87, 6961–7005.
[3] N. A. Tolmachova *et al Chem. Commun.*, **2018**, *54*, 9683–9686.
[4] A. V. Chernykh *et al Org. Biomol. Chem.* **2022**, *20*, 9337–9350.
[5] A. A. Homon *et al Eur. J Org. Chem.* **2021**, *47*, 6580-6590.
[6] I. G. Logvinenko *et al Org. Biomol. Chem.*, **2024**, *22*, 7982-7988.

Radical Photochemical Difluorosulfoximination of Alkenes and Propellanes

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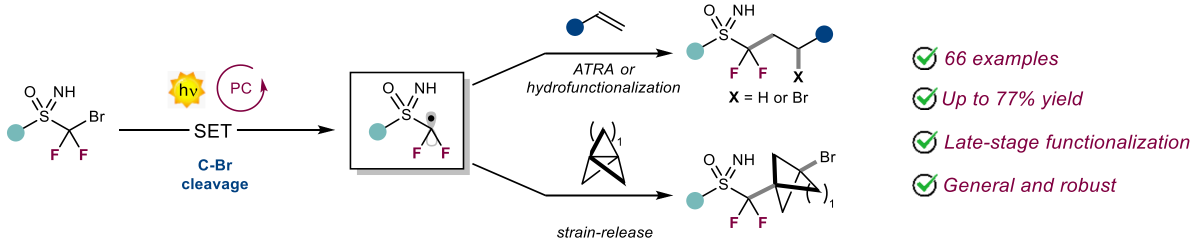
Sulfoximines are promising moieties for their bioisosteric replacement of sulfones.[1] Theses compounds possess interesting properties such as high chemical stability, increased solubility in water and multiple hydrogen bond donor/acceptor sites. Further, the N-atom adds value to the structure from a sulfone by adding intrinsic chirality and the possibility to explore the 3D-chemical space with exit vectors. On the other hand, the unique effect of the fluorine atom on physical and biological properties of chemicals, organofluorine chemistry holds a central role in various areas, with many applications in materials, agrochemical, and medicinal chemistry. Especially in medicinal sciences, the fluorine atom shown in many cases, an increasing bioavailability with respect to their original non fluorinated versions.[2] We thus may hypothesize that S-perfluoroalkylated sulfoximines would have a dual advantage in terms of properties. However, the installation of the sulfoximine unit into a substrate in one pot is quite challenging and not very explored in literature.

Here, we report for the first time, a new method of sulfoximination by C-C bond of olefins and propellanes enabled by a metal-free photocatalysts. The process is general, robust and tolerates diverse functional groups, including esters, ketones, double bond, silyl groups and boronic esters. The rationalization of divergent reaction mechanism performing Stern-Volmer quenching and EPR experiments revealed the key activity of a difluoroalkyl sulfoximine radical.



Scheme 1. Light-driven difluorosulfoximination of alkenes and propellanes

References

[1] Baldone, S.; Paut, J.; Anselmi, E.; Dagousset, G.; Tuccio, B.; Pelosi, G.; Cuadros, S.; Magnier, E.; Dell'Amico, L. *Chem. Sci.* **2025**, *16*, 6957.

Rational Design of Polyfluorinated Peptide-based Biomaterials

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Peptides are particularly appealing to generate efficient nanocarriers for biomedical applications because they can be rationally designed to self-assemble into nanoscale structures. The main advantage of peptides is their diversity, by virtue of side-chain chemistry. Introducing the C-F bond at specific positions influences key properties of amino acids and can be a powerful tool to fine-tune a broad range of properties.[1] In the past two years, we investigated the impact of fluorination on peptide self-assembly and drug delivery performance incorporating tailor-made fluorinated amino acids [2] into a pH-sensitive amphiphilic block co-polypeptide featuring an RGD bioactive motif. We underlined the crucial role of fluorine influencing nanostructure morphology, enhancing drug encapsulation and controlled release efficiency. Additionally, fluorinated peptides exhibit lower cytotoxicity in human cells, compared to their non-fluorinated counterpart, and a tunable enzymatic degradation profile via elastase, dictated by the degree of fluorination. These results underscored fluorination as a powerful tool to precisely control peptide self-assembly, significantly improving structural and biological properties for next-generation nanocarrier development. Herein, we present a new library of polyfluorinated peptide-based materials exchanging the bio-tag of our original motif in order to explore the range of cell receptors that can be targeted. In contrast to the current concerns surrounding per- and polyfluoroalkyl substances (PFAS), our fluorinated peptide materials provide a greener alternative by maintaining superior performance while exhibiting reduced toxicity and enhanced biocompatibility. [3]

References

[1] Berger, A.A., et al., Deciphering the Fluorine Code—The Many Hats Fluorine Wears in a Protein Environment. Acc. Chem. Res., **2017**. 50(9): p. 2093-2103
[2] Hohmann, T., et al., Gram-Scale Asymmetric Synthesis of Fluorinated Amino Acids Using a Chiral Nickel(II) Complex. J. Org. Chem., **2022**. 87(16): p. 10592-10604
[3] Khan, M.F., et al., Biodegradation of Amphipathic Fluorinated Peptides Reveals a New Bacterial Defluorinating Activity and a New Source of Natural Organofluorine Compounds. Environ. Sci. and Technol., **2023**. 57(26): p. 9762-9772.

Towards a New Direct Method for the Synthesis of Aryl Difluoroalkyl Ethers from the Difluoromethoxy (-OCHF$_2$) Moiety

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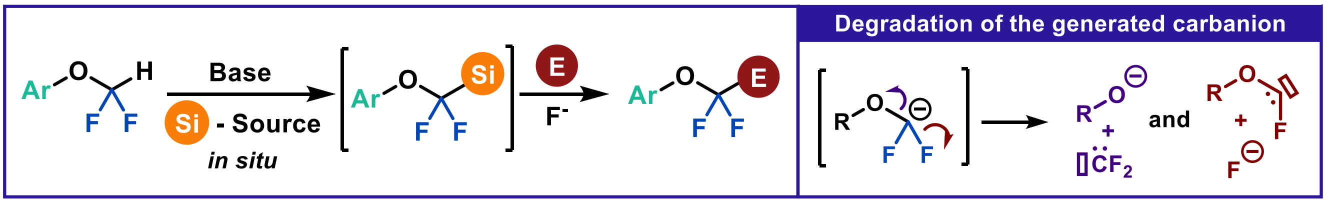
Over the past few years, fluorine chemistry has become an essential component in the synthesis of active medicinal ingredients due to the ability of fluorinated groups to change the physicochemical and **improve biological properties/activity** of molecules compared to their hydrogen-bearing analogues.[1] Among emerging fluorinated motifs, **alkyl** or **aryl difluoroalkyl ethers** (**Alk/Ar-OCF$_2$-R**) could be of particular interest since the difluoroalkoxy motif greatly enhances the metabolic stability of neighbouring benzylic positions with regard to oxidation by CYP450 enzyme in liver, and because they are anticipated to behave as bioisosteres of esters or amides.[2,3] Nevertheless, access to these compounds is still limited to **harsh reaction conditions** using complex or unstable fluorination agents such as XeF$_2$, the desulfurization-fluorination process or strongly acidic conditions and applicable to a **limited scope of substrates**.[4,5] Moreover, many of the reagents relevant to the synthesis of these difluorinated compounds are toxic and dangerous to handle. It is therefore interesting to develop a complementary, **reliable** and **substrate-compatible** method to **facilitate access** to these interesting **alkyl** or **aryl difluoroalkyl ethers**.

A **literature review** for introducing this group will be presented, as well as the **optimization work** and the **scope of application** on a new direct method of accessing this group from the difluoromethoxy moiety. The challenge here is to overcome the high instability of the generated carbanionic species and to bypass the formation of **fluorocarbenes**. For that, **difluorosilylated intermediates** were involved in this two-step reaction sequence to act as masked carbanions and enable their stabilization for further functionalization.[6]



Scheme 1. Our two-step reaction sequence for the **-OCF$_2$H** moiety functionalization.

References

[1] Inoue, M.; Sumii, Y.; Shibata, N. *ACS Omega* **2020**, *5 (19)*, 10633–10640.
[2] Lien, V. T.; Pettersen, S.; Haugen, M. H.; Olberg, D. E.; Maelandsmo, G. M.; Klaveness. *Arch. Pharm.* **2019**, *352 (9)*, e1900101.
[3] Meanwell, N. A. *J. Med. Chem.* **2018**, *61 (14)*, 5822–5880.
[4] Zajc, B.; Zupan, M. *J. Org. Chem.* **1990**, *55 (3)*, 1099–1102.
[5] Kuroboshi, M.; Hiyama, T. *Synlett* **1994**, *1994 (4)*, 251–252.
[6] Guidotti, J.; Metz, F.; Tordeux, M.; Wakselman, C. *Synlett* **2004**, *2004 (10)*, 1759–1762.

PARALLEL SESSION I

Inorganic Chemistry and Computational Chemistry

Chemistry of MoF_5 and $MoOF_3$

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Molybdenum pentafluoride has been shown to form 1:1 and 1:2 adducts with monodentate Lewis bases such as pyridine.[1] The use of polydentate Lewis bases was found to induce autoionization of MoF_5 leading to the formation of $[MoF_6]^-$ salts of fluorido Mo cations (Figure 1). The Mo oxide fluoride $MoOF_3$ forms neutral adducts with monodentate and bidentate Lewis bases. Reactions of neutral adducts of $MoOF_3$ with $SbF_5(SO_2)$ are a synthetic path to Mo oxide fluoride cations. The compounds are characterized by Raman spectroscopy, X-ray crystallography, and Density Functional Theory calculations.

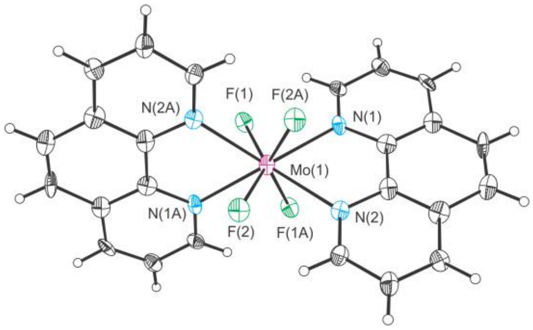

Figure 1. Thermal ellipsoid plot of the $[MoF_4(phen)_2]^+$ cation.

References

[1] Bykowski, J.; Turnbull, D.; Hahn, N.; Boeré, R. T.; Wetmore, S. D.; Gerken, M. *Inorg. Chem.*, **2021**, *60*, 15695-15711.

Metal Fluoride Complexes as Functional, Structure-Directing Building Blocks in Molecular Magnetism and Beyond

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The functional group is an immensely successful concept – possibly the defining one in preparative organic chemistry. However, it is largely lacking in inorganic chemistry. While assembly of discrete coordination complexes into more complicated structures of varying dimensionality is commonplace, the versatility of such approaches nowhere matches the synthetic control which is routine in organic synthesis. In this context, metal fluoride complexes can serve as structure directing building blocks with quite well defined chemical selectivity and geometric preferences.[1-4] Application of this conjecture towards rational assembly of molecule-based magnetic systems will be illustrated sampling the f-block as well as the d-block.

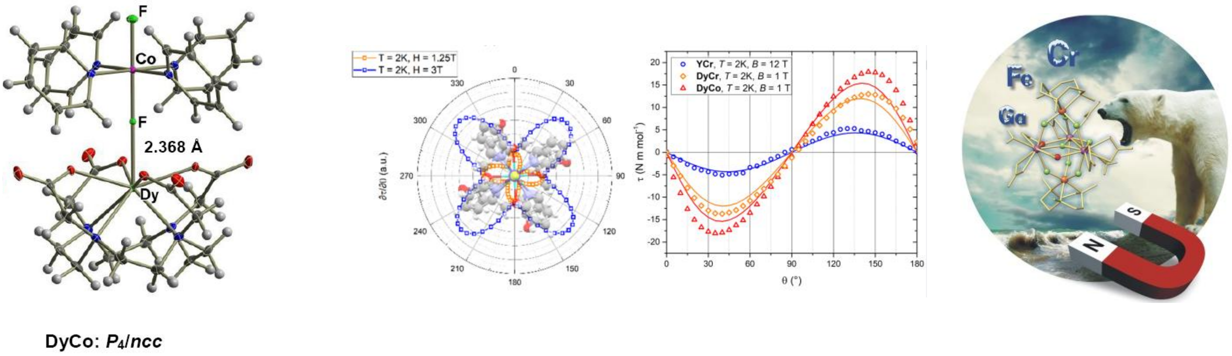

Figure 1. Fluoride mediated magnetic exchange and ligand field effects act as handles for tuning magnetic properties of mixed 3d-4f molecular magnets providing for magnetic anisotropy switches and magnetic coolers.

References

[1] K. S. Pedersen, J. Bendix *et al.*, *Chem. Sci.* 2012*, 3*, 1024-1032.
[2] T. Birk, K. S. Pedersen, J. Bendix *et al. Inorg. Chem.*, 2012, *51*, 5435-5443.
[3] Pedersen, K. S.; Sørensen, M. A.; Bendix, J. *Coordination Chemistry Reviews* 2015, *299*, 1.
[4] Pfleger, R. F.; Briganti, M.; Bonde, N.; Ollivier, J.; Braun, J.; Bergfeldt, T.; Piligkos, S.; Ruppert, T.; Anson, C. E.; Perfetti, M.; Bendix, J.; Powell, A. K. *Chemistry – A European Journal* 2025, *31*, e202403002.

Physicochemical Parameters of Chemical Capacitors Featuring Fluorine-rich Oxidizers and Separators

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University of Warsaw, Centre of New Technologies, Banacha 2C St., Warsaw, Poland
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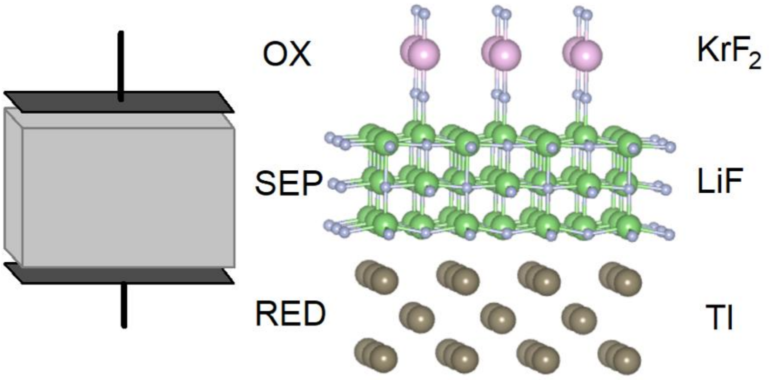
A chemical capacitor (abbrev. *chem-cap*) is a new type of nanostructure proposed in 2021[1-3] (see Scheme 1) with unique physicochemical properties.



Scheme 1. The structure of a classic flat capacitor (left) and a chem-cap on the example of a Tl-LiF-KrF_2 layered system (right). The inert separator (SEP) is middle layer between two other layers of strongly reducing (RED) and oxidizing (OX) substances deposited on its two surfaces.

Taking into account structurally adequate (i.e. meeting the epitaxy condition) F-rich strong oxidants and reducers, and/or F-rich insulating SEP layers, several chem-cap structures were proposed. Their crystal and electronic structures were determined using theoretical methods. The calculations were performed based on density functional theory (DFT) in the VASP package using the GGA Perdew-Burke-Ernzerhof functional in the solid-state version (PBEsol). Then, selected physicochemical properties describing the interactions between the OX and RED layers deposited on both sides of the SEP layer were calculated. The values of charge transfer between layers, electric capacitances, electric potential differences and energies stored in the electric field were determined for these systems.

References

[1] A. Grzelak, J. Lorenzana, W. Grochala, *Angew. Chem. Int. Ed. Engl.*, **2021**, *60*, 13892.

[2] D. Jezierski, et al., *Phys. Chem. Chem. Phys.*, **2022**, *24*, 15705.

[3] W. Grochala, *Wiadom. Chem.*, **2021**, *75*, 755.

Acknowledgements

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Novel Xe−N and Xe−O Bonded Cations: Formation, Structure, and Reactivity

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Binary noble-gas fluorides are key precursors in noble-gas chemistry, and consequently, most noble-gas compounds synthesized in macroscopic quantities feature noble-gas–fluorine bonds. In contrast, Xe−O and Xe−N bonded species are less explored. Lewis acidic XeF^+ salts enable their formation through interactions of suitable oxidatively resistant donor ligands with the σ-hole present on the Xe atom of the XeF^+ cation [1–5]. In this study, carbamoyl fluoride and cyanogen were reacted with $[XeF][AsF_6]$ in anhydrous HF, yielding novel adduct cation salts $[H_2NC(F)OXeF][AsF_6]$ (Fig. 1a) and $[FXeNCCNXeF][AsF_6]_2$, respectively. A fluoride rearrangement of the nearly linear $[FXeNCCNXeF]^{2+}$ cation resulted in formation of $[XeNC(F)C(F)NXe][AsF_6]_2$, a uniquely stable C=N−Xe-bonded species capable of forming N−Xe−N linkages (Fig 1b). These novel compounds were characterized using low-temperature single-crystal and powder X-ray diffraction, low-temperature Raman spectroscopy and studied by quantum-chemical calculations.

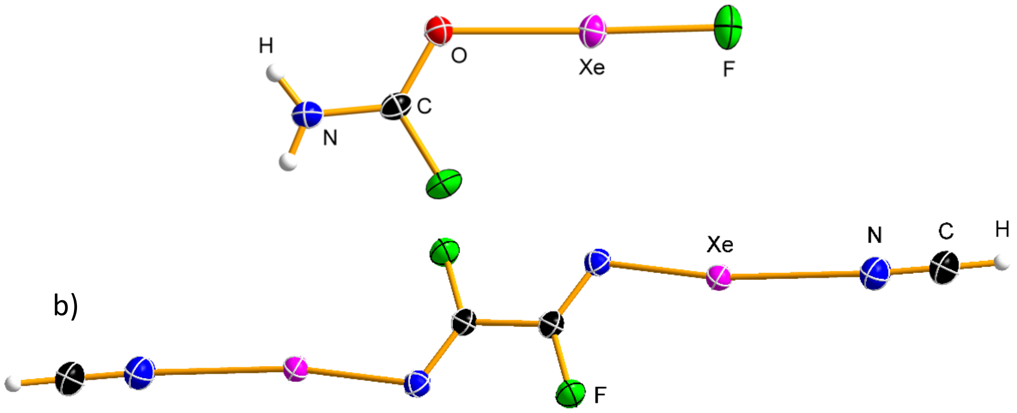

Figure 1. *a)* Crystal structure of the $[H_2NC(F)OXeF]^+$ cation. *b)* N−Xe−N bonding modality observed in the crystal structure of $[HCN\cdots XeNC(F)C(F)NXe\cdots NCH]^{2+}$. The $[AsF_6]^-$ anions are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

References

[1] Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.,* **1974**, *13 (7)*, 1694–1698.

[2] Minkwitz, R.; Molsbeck, W. *Z. Anorg. Allg. Chem.*, **1992**, *612 (6)*, 35–39.

[3] Emara, A. A. A.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.*, **1987** *(21)*, 1644–1646; **1988** *(4)* 257–259.

[4] Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.*, **1988** *(22)*, 1506–1508.

[5] Smith, G. L.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.*, **2007**, *46 (4)*, 1369–1378.

From Copper to Lanthanides: Unique Complexes with Weakly Bound Ligands and Stabilized by Weakly Coordinating Anions

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Development of weakly coordinating anions (WCAs) enabled generation of metal cations in environment of low Lewis basicity. In such conditions cations can form highly reactive or otherwise unstable complexes or can exhibit unusual reactivity in catalytic processes.[1,2]

In this presentation we show our recent contribution to the field of coordination chemistry with main group elements, transition metals and lanthanides which was enabled by the use of perfluorinated WCAs. This includes the synthesis and structural characterization of the first Cu-Xe (Fig. 1) complex, but also alkaline earth metal cations ligated with weakly Lewis-basic molecules. We also present novel lanthanide complexes which could serve as convenient precursors to magnetic materials. Presented compounds are discussed in the context of their crystal structures and stability. Experimental data are complemented with DFT calculations which give insight into electronic structures and bonding energies.

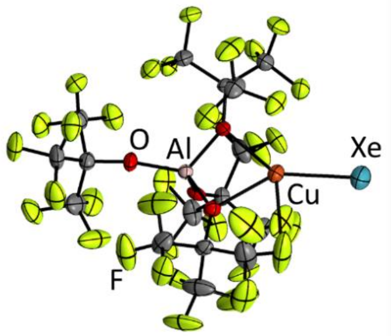

Figure 1. The view of Cu-Xe complex stabilized by $\{Al(OR^F)_4\}^-$ anion ($R^F = C(CF_3)_3$) in the crystal structure.

References

[1] Riddlestone, I. M.; Kraft, A; Schaefer, J.; Krossing, I. *Angew. Chem. Int. Ed.,* **2018**, *57 (43)*, 13982.

[2] Grochowska-Tatarczak, M.; Koteras, K.; Kazimierczuk, K.; Malinowski, P. J. *Chem. Eur. J.*, **2024**, *30 (45)*, e202401322.

Establishing of the Fluorinated Agent Database: Fluobase

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Fluorinated compounds play a crucial role in medicinal chemistry, agrochemicals, and materials science.Consequently, there is an increasing demand for the development of safe, efficient reagents and selective synthetic methodologies for introducing fluorine or fluorine-containing groups into organic compounds. Over the past few decades, a wide variety of shelf-stable fluorinating and fluoroalkylating reagents have been developed. [1] In this presentation, we will discuss our efforts toward: 1) establishing reactivity scales for fluorinating and fluoroalkylating reagents.[2] 2) Establishing a fluorinated reagent database.[3] 3) Applying the fluorinated reagent database for the design of novel reagents.[4]

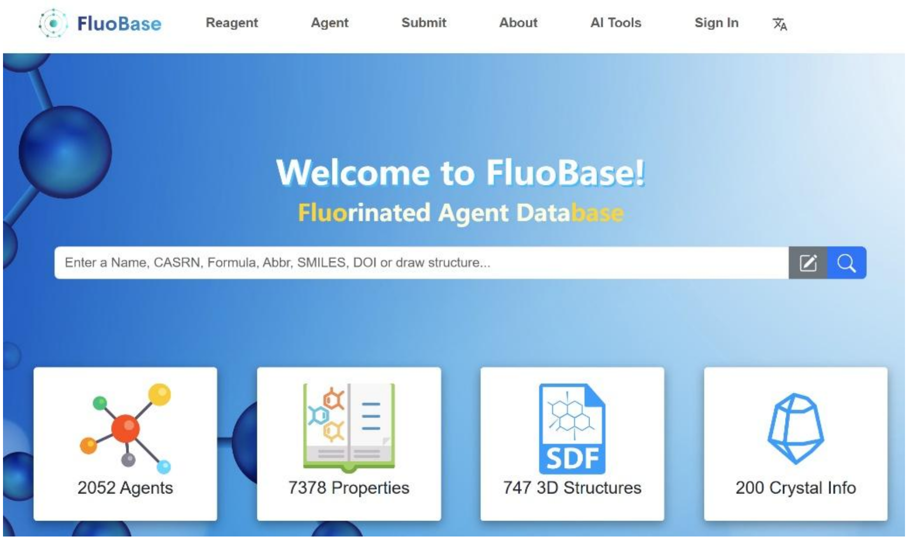

Figure 1. Web: https://fluobase.siochemdb.com/

References

[1] 1 For selected reviews: (a) Ni, C.; Hu, M.; Hu, J., *Chem. Rev.* **2015**, *115*, 765-825; (b) Charpentier, J.; Früh, N.; Togni, A., *Chem. Rev.* **2015**, *115*, 650-682; (c) Shao, X.; Xu, C.; Lu, L.; Shen, Q., *Acc. Chem. Res.* **2015**, *48*, 1227-1236; (d) Shibata, N., *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1307-1320; (e) Chachignon, H.; Cahard, D., *Chin. J. Chem .* **2016**, *34*, 445-454.

2 Li, M.; Xue, X.-S.; Cheng, J.-P., *Acc. Chem. Res.* **2020,** *53*, 182-197. Zheng H., Li Z., Jing J., Xue X.-S., Cheng J.-P. *Angew. Chem. Int. Ed.,* **2021**, 60, 9401.

3 FluoBase: https://fluobase.siochemdb.com/; Y. Li, W. Huang, L. Zhang, D. Su, H. Xu, X.-S. Xue, *Artificial Intelligence Chem.*, **2024**, 2, 100043.; R. Mulka , et. al. Y. Li, X.-S. Xue**,** *J. Cheminformatics,* **2025**, 17, 19.

4 M.-M. Zheng, L. Cai, T. Ma, H.-D. Tan, X. Lai, J. Dong, X.-S. Xue. *Nature Synthesis,* **2024**, 3. 1507.

Decoding the Fluorous Effect with IR Spectroscopy

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Point-side fluorination is a widely used strategy in chemical synthesis to fine-tune the physicochemical properties of molecules. Fluorination is particularly known for increasing hydrophobicity. Perfluoroalkyl moieties, in addition to being hydrophobic, exhibit lipophobicity and a tendency to self-aggregate and phase-separate—a phenomenon commonly referred to as the "fluorous effect." However, fluorinated molecules are also notoriously persistent in the environment, raising concerns about their toxicity and potential for bioaccumulation. These issues arise from the unique van der Waals interactions among fluorinated molecules, which differ fundamentally from those observed in aliphatic compounds. Understanding these interactions is crucial for elucidating toxicity mechanisms, environmental transport dynamics, and bioaccumulation potential.

Infrared spectroscopy (IR) provides a non-destructive method for studying these molecular interactions. In our research, we examine how simple fluorinated molecules respond to different chemical environments using the Vibrational Stark Effect (VSE)[1]. By combining Molecular Dynamics (MD) simulations with IR measurements in various solvents, we have developed calibration curves that allow us to estimate the local electric field experienced by a fluorinated bond based on the peak position of C–F stretching vibrations in an IR spectrum.

In the second part of our talk, we will explore how infrared spectroscopy can be used to detect phase separation and aggregation in fluorinated molecules. Specifically, we will demonstrate how spectral band shapes are influenced by the presence of a fluorous phase.

References

[1] Cruz R.; Ataka K.; Heberle, J., Kozuch, J., *J. Chem Phys*, **2024**, *160* , 20

Superconductivity in Lithium Hydride Layer Enhanced by Fluoride Substrates

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According to World Bank Data, in 2014, 8.25% of the electric energy produced worldwide was used for transmission and distribution of the electric current (Ohmic losses). Reducing this number would benefit both economies and the environment. Thus, intense quest for the new superconducting systems is ongoing.

The chemical composition of the known superconductors is dominated by metals and oxygen or hydrogen. Search of a hydride superconductors was inspired by Ashcroft, who suggested that the covalent nature of bonds in hydride compounds and low mass of hydrogen atoms might help in achieving high-temperature superconductivity.[1, 2] Unfortunately, pressure required to transform hydrides to high-T_C superconductors is enormous. E.g., superconductivity in compressed H_2S and other hydrides was observed at pressures ranging from 100 to 250 GPa.[3] Because of that, practical application of such hydride superconductors is close to impossible at the moment. Another way of achieving superconductivity is by using a "chemical capacitor" setup proposed in 2021.[4] In such a system, a layer of oxidizer and a layer of a reducer are separated by redox-inert layers, causing spontaneous partial transfer of electrons and concomitant metallization of both redox-active layers. Changing the composition of redox layers and the distance between them, one can manipulate the amount of transferred charge.

As we have recently shown, hole doping of a lithium hydride monolayer in the chemical capacitor setup should lead to the appearance of superconductivity.[5] This stems from both the appreciable electron-phonon interaction constant, λ, and substantial density of states on the Fermi level. One might expect that the main contribution to the electron-phonon coupling originates from the lithium hydride layer, for the reasons mentioned by Ashcroft. Surprisingly, it turns out that in some systems, most of the electron-phonon coupling comes from the redox-inert **fluoride** salt, serving as a separator or substrate. In this work, we are taking a closer look at the factors that help fluoride substrates to promote superconductivity in the chemical capacitor setup.

References

[1] Ashcroft, N. W. *Phys. Rev. Let.*, **1968**, 21, 1748.
[2] Ashcroft, N. W. *Phys. Rev. Let.*, **2004**, 92, 187002.
[3] Drozdov, A. P.; Eremets, M. I.; Troyan, I. A.; Ksenofontov, A.; Shylin, S. I. *Nat.,* **2015,** 525, 73.
[4] Grzelak, A.; Lorenzana, D. J.; Grochala, W. *Angew. Chem.*, **2021**, 60, 13892.
[5] Szkudlarek, P. G.; Renskers, C.; Margine, E.R.; Grochala, W., *ChemPhysChem*, **2025**, *submitted*.

PARALLEL SESSION I

Contaminants of Emerging Concern sponsored by MAR2PROTECT

Implementing LivingLabs for Groundwater Protection: MAR2PROTECT Experiences in Europe and Africa

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The relevance of engaging society in environmental issues has been recognised as a critical element for successful environmental management [1; 2]. Among a variety of approaches, Living Labs, typically understood as innovation experiments with a variety of stakeholders in their real-life settings [3], have been gaining increasing attention, especially as their focus has evolved over the past few decades from facilitating technological innovations to addressing societal challenges [4; 5]. This presentation showcases how the promise of LivingLabs as a tool for meaningful stakeholder engagement in innovation processes for urgent environmental challenges can be realised in the 'real-life context' of projects. It offers primary empirical research carried out within the context of the Horizon Europe project MAR2PROTECT (2022-2026). Focusing on Managed Aquifer Recharge (MAR) as a method for alleviating water scarcity, preventing groundwater contamination, and contributing to environmental sustainability, MAR2PROTECT provides a holistic approach to preventing groundwater contamination from the impacts of climate change and global change. Guided by a tailored LivingLabs methodology developed for the project that is able to take into account local contexts, culture and stakeholder relations, six demo sites have set up and implemented a LivingLab. In each of those LivingLabs, diverse stakeholders from the quadruple helix have been engaged in the validation of diverse technological solutions addressing groundwater contamination prevention and remediation as well as the co-design of distinct civil society engagement activities for the prevention of groundwater contamination. The comparative analysis of the implementation of the MAR2PROTECT LivingLabs in distinct geographical, climatic, socio-economic, and political settings provides key insights not only into the extent to which these LivingLabs have been able to achieve their respective objectives but also how these outcomes were achieved. The results provide details of (i) how the tailored LivingLabs methodology and careful knowledge management approaches have served to combine the diverse technical disciplinary expertise among the project partners; (ii) which demand-driven trainings were delivered to strengthen their capacity to implement the LivingLab workshops and stakeholder engagement activities; and (iii) how learning across the project teams behind each LivingLab was continuously fostered, including from the existing stakeholder engagement activities in the Dutch demo site.

References

[1] Lee, H., Calvin, K., Dasgupta, D., Krinner, G., Mukherji, A., Thorne, P., Barret, K. (2023). ClimateChange 2023: Synthesis Report, Summary for Policy makers, Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change IPCC.

[2] O'Connor, R. E., Anderson, P. J., Fisher, A., & Bord, R. J. (2000). Stakeholder involvement in climate assessment: bridging the gap between scientific research and the public. *Climate Research*, 14, 255-260.

[3] Ståhlbröst, A., & Holst, M. (2017). Reflecting on actions in living lab research. *Technology Innovation Management Review*, 7(2), 27-34.

[4] Lakatos, E.S.; Pacurariu, R.L.; Bîrgovan, A.L.; Cioca, L.I.; Szilagy, A.; Moldovan, A.; Rada, E.C. A Systematic Review of Living Labs in the Context of Sustainable Development with a Focus on Bioeconomy. *Earth 2024*, 5, 812-843.

[5] Edwards-Schachter, M. (2019) Living Labs for social innovation, in Atlas of social innovation. 2nd volume: *A world of new practices*, OEKOM: Valencian International University (VIU), (pp.138-143)

Natural Wetlands as Nature-based Solutions to Remove Pollutants and Promote the Good Quality of Estuarine Surface Water

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Natural wetlands, including estuarine saltmarshes, have long been used as uncontrolled discharge sites for different sources of wastewater due to their recognised ability to improve water quality. Saltmarsh plants and their associated microbial communities, along with their sediments, play an important role in the removal of contaminants. Plant roots and rhizomes can act as a net that traps thin sediments leading to a decrease in water flow and turbulence in these areas, resulting in the retention of pollutants in sediments and subsequent accumulation/degradation by marsh vegetation and associated rhizosphere microbial communities. Saltmarsh plants and their rhizosphere microbial communities have proven to be phytoremediation agents for the retention and/or removal of several of these contaminants Estuarine saltmarshes can therefore, act as filters for pollutants released from different anthropogenic activities, including agricultural, industrial and domestic discharges, as many urban areas are located near or within estuaries. Moreover, aquaculture facilities and ports can contribute to the anthropogenic pressures in estuaries. Hence, different contaminants can be found in estuarine environments, namely metals, endocrine disrupting chemicals, pesticides and petroleum hydrocarbons, as well as contaminants of emergent concern (CECs) like pharmaceuticals. Using the Lima estuary (Northern Portugal, Figure 1) as a case study, this presentation will show the potential of saltmarshes to remove various contaminants (e.g., metals, pharmaceuticals and other CECs) from the aquatic environment, preventing them from spreading in the area and reaching coastal areas and/or eventually contaminating the underlying aquifers. The presentation will also outline the innovative approach that is being implemented in the Lima estuary that combines the phytoremediation potential of saltmarsh halophytes with pilot revegetation efforts to enhance the uptake and/or biodegradation of contaminants present in sediments and surface water (Figure 1). All these activities are being developed in the framework of the Mar2Protect EU project. Results will showcase the potential of saltmarsh ecosystems in promoting sustainable water management.

Figure 1. Lima estuary and re-vegetation site.

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Real-time Biomonitoring of Emerging Contaminants in Water Resources

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Engineered microbes coupled to automated IoT devices offer a potentially effective approach for real-time detection of emerging contaminant (EC) in water, which became a global challenge that pose health risks to humans and ecosystems. Current analytical chemistry-based approaches that are applied for EC screening in environmental waters, such as mass spectrometry remain the golden standard, but due to their high cost, requirement for specialized facilities and user expertise, slow turn-around as well as the growing number of EC's to screen for, their application remain limited. Our research explores the use of engineered yeast and algae as part of a real-time EC sensor system in which biofilm 'cell factories' serve as a constant supply of microbes for inline continuous-flow exposure to environmental contaminants. Saccharomyces cerevisiae was stably transformed with genetic circuitry to report the presence of estrogenic ECs as a fluorescence signal, whereas a mutant Chlamydomonas reinardtii strain, as well as a wildtype strain were tested. The system's design enables continuous flow exposure without the need for prefiltration or the risk of modified organisms entering the environment where it is installed, with additional advantages such as low cost and deployable requiring minimal skills. A conceptual framework for groundwater EC monitoring and regulation by public and private sector stakeholders, using engineered microbe-driven IoT devices was incorporated to enable effect-based monitoring at remote locations, and to serve as a platform for further refinements such as microbes with improved sensitivity and novel biological pathways to expand the range of health risks that can be detected.

Integrated Fixed-bed Column Adsorption and Solid-State Fermentation for Effective Removal of Bisphenol A Using Biochar-based Biomaterials

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Tunisia's groundwater resources are increasingly threatened by overexploitation, salinization, and pollution from agricultural and industrial activities. A growing concern is the presence of Contaminants of Emerging Concern (CECs), including endocrine-disrupting chemicals like Bisphenol A (BPA), which originate from non-point source pollution and accumulate in soils and surface waters [1]. These persistent pollutants pose significant risks to both ecosystems and public health, highlighting the urgent need for innovative and sustainable remediation strategies. Biochar has gained attention as a cost-effective and environmentally friendly material due to its high adsorption capacity and potential for pollutant removal [2]. This study focuses on developing advanced biomaterials from agricultural waste, designed to selectively capture and degrade BPA through an integrated approach combining fixed bed column adsorption and biological treatment by solid state fermentation (SSF) using white rot fungi.

Continuous flow fixed bed column tests were performed using palm leaves biochar functionalized with clay (PLC5) for BPA removal. The experiment was conducted with a flow rate of 2 ml/min and an inlet BPA concentration of 10 mg/L. Monitoring was performed until the biochar reached saturation. Breakthrough curves assays showed that saturation by BPA occurs at 42.5 h with a 70% removal capacity. The saturated biochar underwent solid-state fermentation by the white rot fungus *Ganoderma resinaceum*, which has the ability to degrade complex molecules through its enzymatic pool. BPA was found to be tolerated by the fungal strains up to the concentration of 100 mg/L with a tolerance index of 80%.

The SSF experiments were carried out under controlled operating conditions (T°= 28°C, moisture content = 70 %). The enzymatic production of lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase (Lac) was monitored throughout the process. The efficiency of fungi in BPA degradation was assessed, showing a significant increase in laccase activity correlating with BPA breakdown.

These findings highlight the potential of integrating fixed-bed column adsorption with solid-state fermentation as an effective remediation strategy. This process offers a sustainable and eco-friendly approach to address water scarcity while protecting groundwater resources from contamination.

References

[1] Mahjoub, O., Mauffret, A., Michel, C., and Chmingui, W. Use of groundwater and reclaimed water for agricultural irrigation: Farmers' practices and attitudes and related environmental and health risks. Chemosphere, **2022**, Vol. 295, 133945.

[2] Puga, A., Moreira, M.M., Pazos, M., Figueiredo, S.A., Sanromán, M.A., Delerue-Matos, C., Rosales, E. Continuous adsorption studies of pharmaceuticals in multicomponent mixtures by agroforestry biochar. Jour of Envir Chem Eng. **2022**, Volume 10, Issue 1, 106977.

Novel Bio-Based Adsorbents for PFAS Removal: A Life Cycle Assessment Approach

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The increasing concern over per- and polyfluoroalkyl substances (PFAS) in wastewater necessitates sustainable and efficient removal technologies. This study presents a novel adsorption approach using bio-based activated carbon derived from Juncus Maritimus (JM) biomass, compared to conventional granular activated carbon (GAC). A Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) were conducted to evaluate the environmental and economic viability of these adsorbents.

The findings highlight the superior adsorption efficiency of JM-derived carbon for PFAS, surpassing commercial GAC while significantly reducing environmental impacts, particularly in global warming potential. The LCA revealed that JM carbon adsorption had up to 55–70% lower environmental burdens than GAC, primarily due to reduced energy consumption during production. The LCC analysis indicated that, while JM carbon is currently costly at the laboratory scale, its economic competitiveness could improve with industrial-scale production. The study also identified energy consumption as the key environmental hotspot, emphasizing the need for process optimization and renewable energy integration.

This research presents the first LCA/LCC study on Juncus Maritimus-derived carbon for wastewater treatment, demonstrating its potential as a sustainable alternative to conventional adsorbents.

References

[1] Ellis, A. C., Boyer, T. H., Fang, Y., Liu, C. J., Strathmann, T. J. Life cycle assessment and life cycle cost analysis of anion exchange and granular activated carbon systems for remediation of groundwater contaminated by per- and polyfluoroalkyl substances (PFASs). *Water Research*, **2023**, *Volume 243, p. 1-14.*

[2] Moeini M., Modaresahmadi K., Tran T., Reddy K.R. Sustainability assessment of PFAS adsorbents for groundwater remediation. *Materials Today: Proceedings,* **2022**, *Volume 60, p. 2209-2216.*

Characterizing and Assessing Removal Performance of Target Natural Contaminants in a Lake-water Pilot Installation in the Netherlands

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Dunea, a Dutch water supplier, utilizes Managed Aquifer Recharge (MAR) as a key process in its production by infiltrating water through open ponds and deep wells. Due to the growing water demand, Dunea is evaluating Lake Valkenburg (LV) as a new potential water source to increase its production and it is testing two pre-treatment options in a pilot plant (16 m^3/h): 1) Coagulation (Coag), Flocculation (Floc), Dissolved Air Flotation (DAF), and Rapid Sand Filtration (RSF), and 2) Coag, Floc, DAF, Ultrafiltration (UF), and Reverse Osmosis (RO). As the produced water is intended for RO feedwater and infiltration purposes, this study compared the two alternatives in terms of water quality, targeting the risks of clogging of the infiltration wells and fouling of the RO system. Additionally, the full scale Coag/Floc/DAF, the newest technologies installed, required optimization for both applications.

In this work, the modified fouling index (MFI-0.45), the modified fouling index-ultrafiltration (MFI-UF) and other water quality parameters, such as dissolved organic carbon (DOC) and assimilable organic carbon (AOC), PFAS, Chlorophyl-a, and biomass were monitored in both pre-treatment lines over time and under different operational conditions, as well as in the water infiltrated through ponds and wells.

The findings showed that the Coag/Floc/DAF/UF achieve higher removal efficiencies of MFI-UF and MFI-0.45 than the Coag/Floc/DAF/RSF. However, in both treatment lines, the DOC removal is insufficient to minimize RO fouling and well clogging risks as per current guidelines. From the operational conditions tested in the Coag/Floc/DAF, higher removals of particulate matter were found with flocculation mixing intensities (G) below 167 1/s, a DAF recirculation rate of 20%, and a coagulant dosage of 25 mg/L. However, further research is needed to determine the final optimal settings. For the RO, a cleaning in place (CIP) frequency of 2.7 months was predicted considering the particulate fouling, and it was recommended an MFI-UF < 1,100 s/L^2 in the RO feedwater for a CIP every 3 months or more. Biological and organic fouling cannot be discarded in the RO. PFAS concentration in lake water is below the current limitations and is effectively removed by the RO process. The physical clogging rate in wells resulted in the lowest with the UF permeate, but further DOC removal should be achieved before well infiltration. The RSF produces water of insufficient quality for deep well infiltration, but it can be utilized for infiltration in ponds. Further validation of the clogging predictions and investigation into other clogging causes is recommended.

Removal of Per- and Poly-fluoroalkyl substances (PFAS) and Pharmaceuticals onto Activated Carbon from Wastewater Effluents

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Per- and polyfluoroalkyl substances (PFAS) are persistent chemicals. Their toxicity and bioaccumulation make them harmful. High exposure to these compounds increases the risk of dangerous health problems for human beings [1]. In addition, pharmaceutical micropollutants are contaminants of emerging concern because they are continuously released into the environment[2]. This poses a long-term problem for human health and the environment. Activated carbons (AC) prepared from biomass waste are efficient and versatile biomaterials for removing contaminants. In order to implement adsorption processes on an industrial scale, this study involved the selection of 3 PFAS (perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS) and perfluoropentanoic acid (PFPeA)) and 3 pharmaceuticals (diclofenac (DCF), valsartan (VAL) and iopromide (IOP)) to evaluate their performance on fixed-bed columns using a biomaterials / activated carbons (ACs) synthesized from biomass waste. The adsorption processes of these systems and their breakthrough curves were determined. The experimental results were compared to a commercially available activated carbon, NORIT demonstrating the best performance of these novel biomaterials. Synthetic water matrices and real water samples from a wastewater treatment plant effluent were used in the experiments. This work contributes to the removal of very important contaminants of emerging concern.

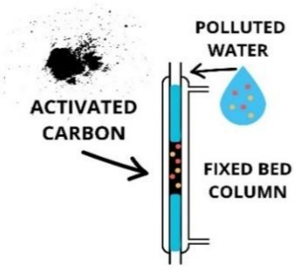

Figure 1. Fixed bed column used for PFAS and pharmaceuticals breakthrough tests.

References

[1] R.A. Dickman, D.S. Aga, A review of recent studies on toxicity, sequestration, and degradation of per- and polyfluoroalkyl substances (PFAS), J Hazard Mater 436 (2022). https://doi.org/10.1016/j.jhazmat.2022.129120.

[2] G. Nazari, H. Abolghasemi, M. Esmaieli, E. Sadeghi Pouya, Aqueous phase adsorption of cephalexin by walnut shell-based activated carbon: A fixed-bed column study, Appl Surf Sci 375 (2016). https://doi.org/10.1016/j.apsusc.2016.03.096.

Suitability and feasibility mapping to assess managed aquifer recharge solutions to cope with groundwater pollution

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Groundwater pollution by emerging contaminants is a major concern for world population because of its toxicity to human health and the environment, and the importance of this source of freshwater for the water supply of cities and agriculture. Its origin is mainly related to human activities: household products (Personal Care Products, detergents, disinfectants), pharmaceuticals, industrial chemicals or agriculture among others. These products are disposed of in the sewage systems and, subsequently in wastewater treatment plants and then, discharged to the environment.

To reduce groundwater pollution there are several solutions that can be applied. The use of managed aquifer recharge (MAR) techniques can be used as a barrier for pollutants to reach the aquifer and, consequently, water supply and dependent ecosystems (wetlands, estuaries, etc.), especially when these techniques are combined with other pre-treatment processes (Mumber *et al*., 2024[1]). Within this framework the HORIZON EU MAR2PROTECT project is working to provide a holistic approach to prevent groundwater contamination from the impacts of climate change and global change, using different innovative technologies, which includes a decision support system (DSS). This DSS will, among others, use spatially distributed data using GIS software to assess the optimal location for two MAR techniques (infiltration ponds and ASR/ASTR -aquifer storage/transfer and recovery-), in terms of the physical (suitability) and technical/economic (feasibility) conditions.

In this work, the results of a methodology for mapping MAR suitability and feasibility areas in several demo sites will be presented. The methodology has been adapted from another EU project (PRIMA AGREEMAR), which took into consideration the most up-to-date methodologies throughout Europe (Martins *et al*., 2024[2]). In the MAR2PROTECT project this methodology has been adapted by simplifying and reducing some of the variables trying to find an improved replicability in other countries, so a scalable solution can be implemented in the DSS.

The main outcomes of the adapted methodology show that, although losing some level of detail in the territory (due to a lower resolution of some of the data), logic and coherent suitability and feasibility areas for MAR are detected. In this sense, areas where nice hydraulic properties exist, together with low water availability and high water demand, are going to be more suitable for MAR solutions, as well as those areas where potential pollution can exist (e.g. agricultural areas).

References

[1] Mumber, T.; Ahrens, L.; Wanner, P. *Managed aquifer recharge as a potential pathway of contaminants of emerging concern into groundwater systems – A systematic review, Chemosphere* ***2024****, 364 (143030)*

[2] Martins, T.N.; Leitão, T.E.; Oliveira, M.M.; Panagiotou, C.F.; Stefan, C.; Chkirbene, A.; Portela, M.M. *Groundwater for Sustainable Development,* ***2024****, 26 (101280)*

Pharmaceutical Removal from Wastewater by Adsorption on Commercial Materials and Molecularly Imprinted Polymers

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This study focused on the development of an adsorption/desorption process as effective technology for pharmaceutical removal from wastewater. The target pharmaceuticals selected are ibuprofen, diclofenac and carbamazepine, while the sorbent materials tested are two commercial ones, an activated carbon Norit 1240W, typically used in wastewater treatment [1], and the non-ionic resin XAD16N, as well as Molecularly Imprinted Polymers (MIPs). Firstly, a sorbent screening phase was conducted in batch mode showing the effectiveness of commercial sorbents and of one MIP for CBZ, that is MIP_CBZ_MAA_TRIM. Then, 3 continuous flow tests were performed with CBZ using the 3 most promising materials previously selected at the same operating conditions, that are Empty Bed Contact Time (EBCT) = 3 min and a bed height of about 20 cm. The breakthrough curves obtained are showed in Figure 1: the MIP for CBZ got saturated after only 3000 BVs, while Norit and XAD16N achieved a 20% breakpoint (BP) at about 18500 Bed Volumes (BVs) of treated wastewater; moreover, XAD16N showed a higher operating capacity (12.4 $mg/g_{dry\ sorbent}$) with respect to Norit (7.1 $mg/g_{dry\ sorbent}$), resulting in a very promising material. The possibility of in situ sorbent regeneration was studied testing the effectiveness of 3 different solvents that are methanol, ethanol and 2-propanol. The analysis revealed that XAD16N can be easily regenerated with 10 to 17 BVs of solvent, depending on the target micropollutant, and among the tested solvents, ethanol is the most promising in terms of consumption and efficiency. Eventually, this study demonstrated the effectiveness of XAD16N and Norit in removing pharmaceuticals from wastewater, with the possibility of *in-situ* regeneration of XAD16N with a very limited amount of ethanol. This work represents a relevant progress towards the development of a reliable and cost-effective adsorption/desorption process.

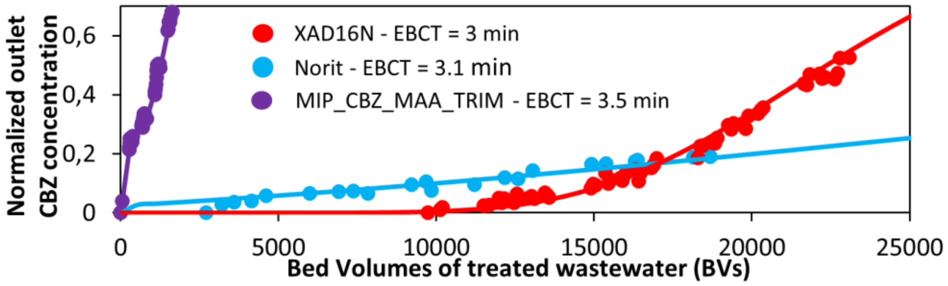

Figure 1: Carbamazepine breakthrough curves experimental data and best-fitting simulations performed with Aspen Adsorption.

References

[1] Benstoem, F., Nahrstedt, A., Boehler, M., Knopp, G., Montag, D., Siegrist, H., Pinnekamp, J., Performance of granular activated carbon to remove micropollutants from municipal wastewater - A meta-analysis of pilot- and large-scale studies. *Chemosphere,* 2017, **185**, 105–118.

PFAS Optical Detection Approach in Mar2Protect

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Mar2Protect project is a European project, funded by the European Union that aims to give a holistic approach for the water protection. This project has several demosites selected due to climatic conditions, water sources and pollution type. One of the objectives is to monitor contaminants relevant to each demosite and the per- and polyfluoroalkyl substances (PFAS) are one of the contaminants under study. PFAS are a group of fluorinated, organic compounds with stable carbon-fluoride bonds [1].The most common detection methods are laboratorial methods with high associated costs, time-consuming and unsuitable for in-situ analysis. It is therefore important to develop sensors for the detection and real-time monitoring of PFAS that can allow quick analysis and simple operation [2]. Optical sensors can be a suitable approach for in-situ monitoring since it allows compactness, lightweight, immunity to electromagnetic interference and also multiplexing capabilities [3]. In this work, the Mar2Protect approach for the detection and monitoring of PFAS will be shown. The proposed approach is a combination between a selective layer developed by FCT NOVA and an optical sensor setup developed by IT. Considerations for the upscaling from the laboratory to the field will also be shown, aiming the sensor implementation to one of the project demosites.

Acknowledgements

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This work was supported by FCT - Fundação para a Ciência e Tecnologia, I.P. by project reference UIDB/50008, and DOI identifier 10.54499/UIDB/50008.

References

[1] Thompson D., Zolfigol N., Xia Z., Lei Y., Recent progress in per- and polyfluoroalkyl substances (PFAS) sensing: A critical mini-review, Sens. Actuators Rep., **2024**, 7 (100189), https://doi.org/10.1016/j.snr.2024.100189.

[2] Rodriguez K.L., Hwang J.H., Esfahani A.R., Sadmani A.H.M.A., Lee W.H., Recent developments of PFAS-detecting sensors and future direction: A review. Micromachines (Basel), **2020**, *11 (667)*, 1-23, https://doi.org/10.3390/mi11070667.

[3] Pires Duarte D. A., Nogueira R. N., Bilro L., Optical Fiber Sensing Principles. Plastic Optical Fiber Sensors, Science Technology and Applications, CRC Press, **2019**, 67–91, https://doi.org/10.1201/b22357-3.

PARALLEL SESSION II

Inorganic Chemistry

A Potpourri of Main-Group Fluorine Chemistry

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The Thrasher Group, including collaborators, is working primarily in two areas of research: (1) new halogen bonding motifs in perfluoroorganic disulfonyl halides, $XO_2SR_FSO_2X$ (where X = Cl, Br, and I), and (2) derivative chemistry of bis(trifluoromethyl)amine, $(CF_3)_2NH$, aimed at the incorporation $(CF_3)_2N$– groups into more complex organic molecules. In the former project, recent efforts to go beyond our published structures on α,ω-di(sulfonyl bromide) perfluoroalkanes [1] to perfluoroaromatic analogues with either tetrafluorophenyl or octafluorobiphenyl spacers will be presented, among other results. In the latter project, since we have yet to find the right conditions for successful hydroamination reactions of $(CF_3)_2NH$, we will present results from our studies on the derivative chemistry of bis(trifluoromethyl)amino carbamoyl fluoride, $(CF_3)_2NC(O)F$. The compound $(CF_3)_2NC(O)F$ has been previously reported by DesMarteau and coworker [2], and we will use either the method of Hu [3] and/or Schoenebeck [4] to generate carbonyl fluoride, $C(O)F_2$, for immediate use in its synthesis from the amine $(CF_3)_2NH$. By way of a further example, we hope to produce the corresponding formamide $(CF_3)_2NC(O)H$ in high yield. This formamide has only been observed in low yields from the pyrolysis of more complex molecules [5] or it has recently appeared in a U.S. patent application on battery electrolytes [6], but otherwise an effective synthesis of this compound remains inaccessible.

References

[1] Wacha, M.; Helm, D. L.; Smart, M. M.; McMillen, C. D.; Casabianca, L. B.; Sachdeva, R.; Urick, C. R.; Wilson, L. P.; Thrasher, J. S. A new motif in halogen bonding: Cooperative intermolecular S–Br···O, O···F, and F···F associations in the crystal packing of α,ω-di(sulfonyl bromide) perfluoroalkanes. *Chem. Asian J.* **2023**, *18*(6), e202300012.
[2] DesMarteau, D. D. Lu, C. Synthesis of *N,N*-bis(trifluoromethyl)amino difluoromethylene trifluorovinyl ether. *J. Fluorine Chem*. **2011**, *132*, 1194 – 1197.
[3] Zhou, M.; Ni, C.; Zeng, Y.; Hu, J. Trifluoromethyl Benzoate: A Versatile Trifluoromethoxylation Reagent. *J. Am. Chem. Soc.* **2018**, *140*(22), 6801 – 6805.
[4] Turksoy, A.; Scattolin, T.; Bouayad-Gervais, S.; Schoenebeck, F. Facile Access to $AgOCF_3$ and Its New Applications as a Reservoir for OCF_2 for the Direct Synthesis of *N*-CF_3, Aryl or Alkyl, Carbamoyl Fluorides. *Chem. Eur. J.* **2020**, *26*(10), 2183 – 2186.
[5] Coy, D. H.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. Polyfluoroalkyl Derivatives of Nitrogen. Part XL. Reaction of Trifluoronitrosomethane with *N,N*-Bistrifluoro-methylamino-substituted Allenes. *J. Chem. Soc., Perkin Tran. 1* **1973**, 1561 – 1564.
[6] Xu, Y.; Yonemoto, B.; Jiang, H. Electrolyte for Secondary Battery and Secondary Battery Including Same. U.S. Patent Appl. 2024/0372141, Nov. 7, 2024 (assignee Microvast, Inc.).

Investigation on the Pentafluorooxosulfate (-OSF_5) Group for Inorganic and (Bio)organic applications

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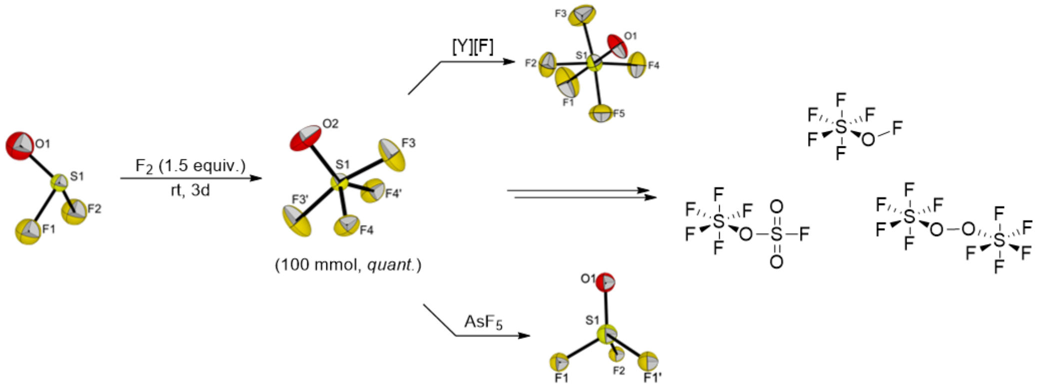
Herein, we report our latest advances concerning the preparation of OSF_5 containing species. First, we re-investigated the synthesis of thionyl tetrafluoride (SOF_4) and its derivatization in the emerging pentafluorooxosulfate [cat][OSF_5] anions.[1-3] From SOF_4, lower fluorinated analogue (SOF_3^+, trifluorosulfoxonium) and higher ($FOSF_5$, pentafluorooxosulfate hypofluorite) were obtained. For the later, we refined its spectroscopic datas and pursued in the journey of finding pentafluorooxosulfate transfer reagents. Here, the ongoing chemistry of the fluorosulfate pentafluorooxosulfate (FSO_2–OSF_5) and related SuFEx reactivity in addition to modern peroxide (F_5SO–OSF_5) activation is highlighted.



Scheme 1. Overview of the reported sulfur oxyfluoride chemistry. From thionyl tetrafluoride preparation to its higher fluorinated analogues (OSF_5, pentafluorooxosulfate) and their use as transfer reagents.

References

[1] J. S. Sturm, A. Millanvois, C. Bahri, P. Golz, N. Limberg, A. Wiesner, S. Riedel, *Chem. Eur. J.* **2024**, *30*, e202403365

[2] A. Haupt, D. Duvinage, E. Lork, M. Ponomarenko, G.-V. Röschenthaler, *Angew. Chem. Int. Ed.* **2021**, 60, 17866

[3] Y. Kraemer, A. M. Stephens, J. A. Buldt, A. Young, C. P. McLoughlin, J. C. Fettinger, L. M. Holder, C. R. Pitts, *Chem. Commun.*, **2025**, 61, 3159-3162

Solubility Investigation of Selected RE_2O_3 in $(LiF\text{-}NaF)_{eut}$ vs $(LiF\text{-}NaF\text{-}REF_3)$ Molten Systems

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Rare earth (RE) elements play important role in the material chemistry and this fact causes a constant increasing demand of these metals. European Union (EU) suffers from the lack of raw materials in general, RE elements including. These elements belong to the group of critical raw materials defined by the EU with very low recycling level [1]. The recycling seems to be the efficient way how to reduce the dependence on imports of raw materials, reduce the volume of waste and how to increase the sustainable development.

Molten salt electrolysis is an industrial method for the extraction of RE elements from corresponding mixtures, including oxides. It is known that the solubility of rare earth oxides (REO) is not high but the presence of RE fluorides increase the solubility.

Our recent work was focused on solubility study of selected RE_2O_3 in the molten mixture of LiF-NaF-REF_3. The composition of LiF-NaF-REF_3 was constant with the lowest temperature of primary crystallization obtained in previous studies. To see the positive effect of REF_3 presence on solubility of RE_2O_3, the experiments on solubility of REO were performed also in the LiF-NaF eutectic mixture. The solubility investigation was measured by thermal analysis of molten mixtures and XRD analysis of the solidified samples. Solubility limit was finally determined based on the presence of RE_2O_3 patterns in the XRD records of solidified mixtures.

Acknowledgements

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References

[1] https://eur-lex.europa.eu/legal-content/SK/TXT/?uri=CELEX:52020DC0474.

New Boryl and Diborate Dianions

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Cyanoborates represent an important class of compounds that are of interest for materials science and synthetic chemistry.[1,2] Especially, the cyanoborate anions $[B(CN)_4]^-$ and $[BF(CN)_3]^-$ have been in the focus due to their use as building blocks in low viscosity RTILs and as starting materials for the boron-centered nucleophile $[B(CN)_3]^{2-}$, which could be synthesized via reduction of $[B(CN)_4]^-$ and $[BF(CN)_3]^-$.[3,4] Besides the 9H-9-borafluorene dianion,[5] $[B(CN)_3]^{2-}$ is the only known dianionic boryl anion known to date and it exhibits a large scope of reactivity.[4,6,7]

Recently, we delevoped a series of organylfluorocyanoborates that were synthesized from the commercially available chemicals $K[RBF_3]$ ($R = CH_3$, $H_2C{=}CH$, Ph, TMSC≡C, PhC≡C) and trimethylsilyl cyanide.[8] The new borate anions served as percursors for new boryl dianions $[RB(CN)_2]^{2-}$, which are accessible by two electron reduction with potassium napthalenide. The obtained dianionc boryl anions $[RB(CN)_2]^{2-}$ readily reacted with hexafluorobenzene and fluorocyanoborates yielding (perfluoroaryl)organylcyanoborates and organyldiborate dianions, respectively. Furthermore, the alkynyl substituents in organyldiborate dianions are well suited for functionalization of the triple bond via Sonogashira cross-coupling reactions (Fig. 1).

Figure 1. Colored dianionic boryl anions $K_2[RB(CN)_2]$ (middle) and crystal structures of triple-bond-functionalized diborate dianions.

References

[1] Ignat'ev, N. V.; Finze, M.; *Eur. J. Inorg. Chem.* **2019**, 3539–3560. [2] Huang, Z.; Wang, S., Dewhurst, R. D.; Ignat'ev, N. V.; Finze, M.; Braunschweig, H.; *Angew. Chem. Int. Ed.* **2020**, *59*, 8800–8816. [3] Bernhardt, E.; Bernhardt-Pitchougina, V.; Willner, H.; Ignat'ev, N. V.; *Angew. Chem. Int. Ed.* **2011**, *50*, 12085–12088. [4] Landmann, J.; Sprenger, J.A.P.; Bertermann, R.; Ignat'ev, N. V.; E.; Bernhardt-Pitchougina, V.; Bernhardt, E.; Willner, H.; Finze, M.; *Chem. Commun.* **2015**, *51*, 4989–4992. [5] Gilmer, J.; Budy, H.; Kaese, T.; Bolte, M.; E.; Lerner, H.-W.; Wagner, M.; *Angew. Chem. Int. Ed.* **2020**, *59*, 5621. [6] Landmann, J.; Hennig, P.T.; Ignat'ev, N. V.; Finze, M.; *Chem. Sci.* **2017**, *8*, 5962–5968. [7] Landmann, J.; Sprenger, J.A.P.; Hailmann, M.; Bernhardt-Pitchougina, V.; Willner, H.; Ignat'ev, N. V.; Bernhardt, E.; Finze, M.; *Angew. Chem. Int. Ed.* **2015**, *54*, 11259–11264. [8] Schopper, N.; Zapf, L.; Sprenger, J.A.P; Ignat'ev, N. V.; Finze, M.; *Chem. Commun.* **2022**, *58*, 1223–1226.

Crystal Structure Elucidation of Xenon Compounds by 3D Electron Diffraction on Nanometer-Sized Crystallites

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Single-crystal X-ray diffraction (SCXRD) is the gold standard for structural characterization, providing definitive chemical structure confirmation [1]. However, obtaining sufficiently large and high-quality single crystals for SCXRD analysis remains a challenge. An alternative approach, 3D electron diffraction (3D ED), allows for crystal structure determination on nanometer-sized crystallites [2]. While the application of 3D ED is rapidly expanding, most reported structures pertain to air-stable compounds, with comparatively little focus on reactive and air-sensitive materials [3].

In this study, a procedure for sample handling and transfer was developed to facilitate the safe manipulation of highly reactive, strongly oxidizing, and air-sensitive compounds [4,5]. This approach enables the secure transfer of such materials onto a transmission electron microscope (TEM) grid, which is mounted in a cryo-transfer tomography holder, allowing their introduction into the TEM without significant degradation. The method was successfully applied to reactive xenon compounds, with their crystal structures determined using low-temperature 3D electron diffraction on nm-sized crystallites. The results were validated by comparison with low-temperature SCXRD data. This technique offers a versatile solution for 3D ED investigations of air-sensitive and reactive compounds that pose challenges for crystal growth and SCXRD analysis.

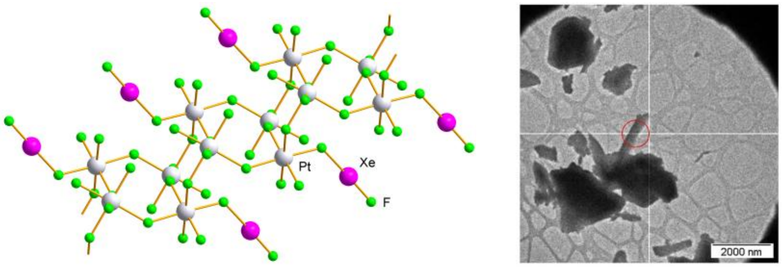

Figure 1. Crystal structure of $XeF_2{\cdot}2PtF_4$ (left) determined by 3D ED on the nm-sized crystallite (right).

References

[1] Bond, A. D. *Resonance*, **2014**, *19 (12)*, 1087–1092.

[2] Gemmi, M.; Mugnaioli, E.; Gorelik, T. E.; Kolb, U.; Palatinus, L.; Boullay, P.; Hovmöller, S.; Abrahams, J. P. *ACS Cent. Sci.*, **2019**, *5 (8)*, 1315–1329.

[3] Jones, C. G.; Asay, M.; Kim, L. J.; Kleinsasser, J. F.; Saha, A.; Fulton, T. J.; Berkley, K. R.; Cascio, D.; Malyutin, A. G.; Conley, M. P.; Stoltz, B. M.; Lavallo, V.; Rodríguez, J. A.; Nelson, H. M. *ACS Cent. Sci.*, **2019**, *5 (9)*, 1507–1513.

[4] Motaln, K.; Gurung, K.; Brázda, P.; Kokalj, A.; Radan, K.; Dragomir, M.; Žemva, B.; Palatinus, L.; Lozinšek, M. *ACS Cent. Sci.*, **2024**, *10 (9)*, 1733–1741.

[5] Gurung, K.; Uran, E.; Motaln, K.; Brázda, P.; Radan, K.; Lozinšek, M.; Palatinus, L. *J. Appl. Cryst.*, **2025**, *58 (3)*, 1079–1084.

Organylpentafluorophosphate Ions

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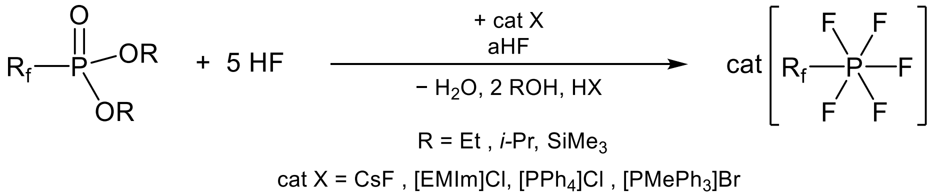
To prepare organylpentafluorophosphates ($[PF_5R_f]^-$), organylphosphonic acid derivatives ($R_fP(O)(OR)_2$) were treated with anhydrous HF (aHF). Oxonium salts of the corresponding $[PF_5R_f]$-phosphates are generated in solution.[1,2] If the phosphonic acid derivatives are introduced with a halide salt (cat X), aHF, water and other by-products can be separated in vacuo after the reaction has taken place. The $cat^+ [PF_5R_f]^-$ salts obtained are thus accessible with a large number of cations in high yield and purity, and each has been fully characterized.



Scheme 1. Synthesis of organylpentafluorophosphate salts from organylphosphonic acid derivatives with halide salts and anhydrous HF.

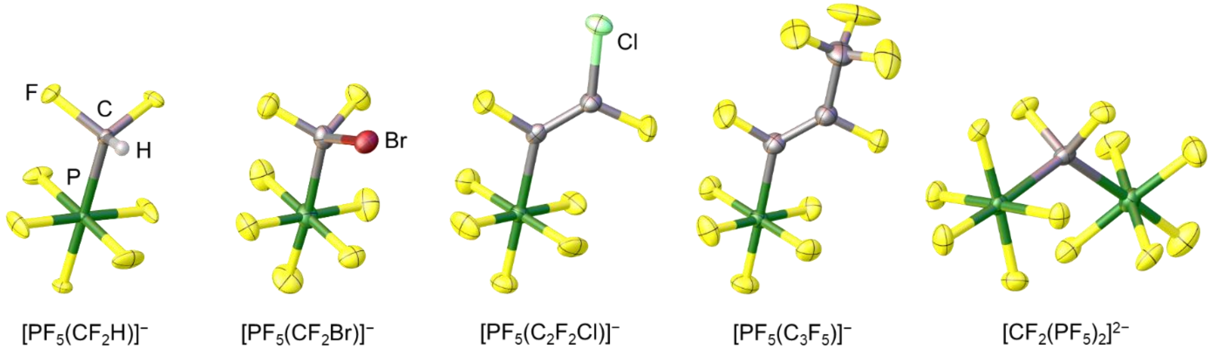


Figure 1. Solid state structures of selected organylpentafluorophosphate salts.

References

[1] N. Ignatyev, U. Welz-Biermann, M. Schmidt, A. Kucheryna, H. Willner, *WO **2005** 049628 A1*, Merck Patent GmbH, Darmstadt.

[2] N. Ignatyev, P. Barthen, K. Koppe, W. Frank, *WO **2016** 074757 A1*, Merck Patent GmbH, Darmstadt.

Autocatalytic Degradation of the Extremely Potent Greenhouse Gas SF_6 in Basic Alcoholic Solution

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Sulfur hexafluoride (SF_6) is an extremely potent greenhouse gases (GWP_{100} of SF_6 is 26700) and is mainly used in the electrical energy sector as a nontoxic and self-healing insulating gas. As part of the efforts to create a green electricity grid, the use of SF_6 is increasingly being regulated and more climate-friendly alternatives are being demanded.[1] Accordingly, there is an urgent need for innovative decomposition processes to prevent the end-of-life-SF_6 from being released into the atmosphere. A wide range of different methods are proposed for the decomposition of SF_6.[2] However, the challenge remains to find a technically simple, fast and low-energy process for the degradation of SF_6. We herein report an easy-to-apply method for the degradation of SF_6. The photochemical process decomposes SF_6 in basic alcoholic solution to afford a mixture of salts containing metal fluorides and sulfites (see Figure 1). Two operational methods were identified which may offer distinct advantages in terms of selectivity, product separation or reaction scale-up. The influence of the base, the alcohol, the irradiation source and the operational method on the reaction rate is discussed and a reaction mechanism is proposed. Current attempts to optimize the system with respect to selectivity and degradation rates are presented which culminates in the degradation of 20 g SF_6 batches with a degradation rate of up to 12 g/h and an energy efficiency of 100 g/kWh.

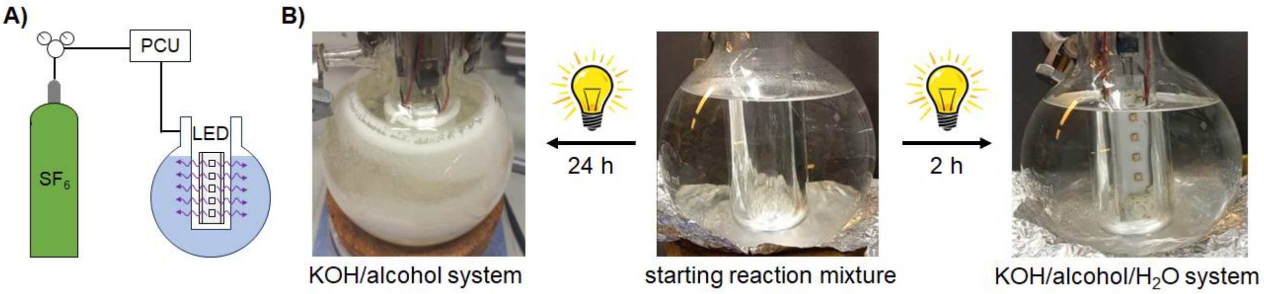

Figure 1. A) Schematic reaction setup (PCU = pressure control unit); B) Reaction vessel containing the reaction mixture (middle) and the KOH/alcohol system (left) and the KOH/alcohol/H_2O system (right) after irradiation.

References

[1] Regulation, EU, 2024. No 573/2024 of the European Parliament and of the Council of 7 February 2024 on Fluorinated Greenhouse Gases and Repealing Regulation (EU) No 517/2014. OJEU.

[2] Zhaolun Cui, Z. C., Yi Li, Y. L.; Song Xiao, S. X.; Shuanngsuang Tang, S. T.; Ju Tang, J. T.; Yanpeng Hao, Y. H.; Xiaoxing Zhang, X. Z. *Sci. Total Environ.* **2024**, *906*, 167347.

Copper(I) Complexes with Weakly Basic Ligands: Exploring Cu(I) Interactions with Dinitrogen and Fluorinated Arenes

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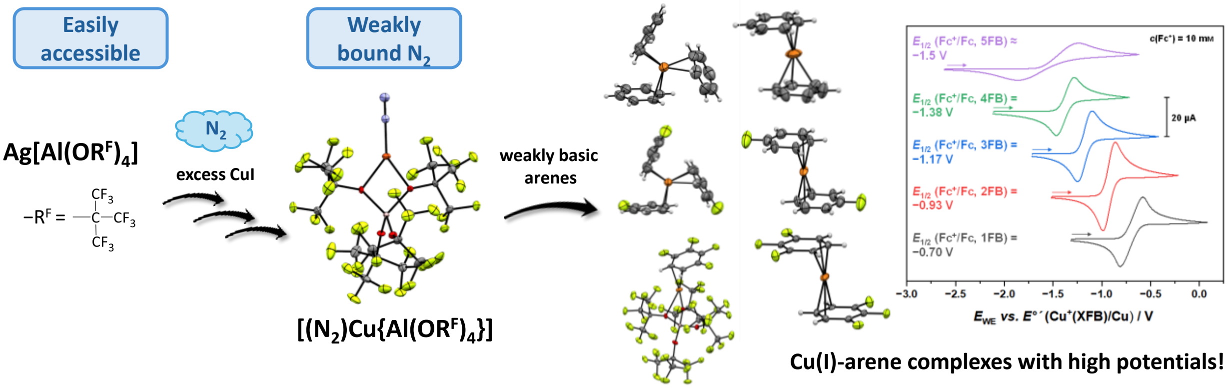
Complexation of weakly basic ligands is often hampered by various competing processes, such as coordination of the solvent or the counter-ion. These undesired reactivities can be avoided by inducing *pseudo gas-phase conditions* using highly fluorinated, and thus weakly coordinating, anions and/or solvents.
Making use of the perfluoro alkoxy aluminate $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) and the solvent *iso*-perfluorohexane, the Cu(I) dinitrogen complex $[(N_2)Cu\{Al(OR^F)_4\}]$ was obtained by a cascade metathesis reaction between the silver salt $Ag[Al(OR^F)_4]$ and excess copper iodide.[1] In this compound, the dinitrogen ligand is barely coordinated which is reflected by its unprecedentedly high N≡N stretching vibration frequency of 2314 cm^{-1}.[1] The weak coordination of N_2 makes $[(N_2)Cu\{Al(OR^F)_4\}]$ the ideal precursor for the syntheses of further weakly coordinated Cu(I) complexes. In (fluorinated) arenes, which are often used as weakly coordinating solvents,[2] homoleptic Cu(I) arene complexes formed and were structurally characterized. The levelling effect of the arene ligands on the copper redox potential was investigated by cyclic voltammetry, revealing high potentials for the strongly fluorinated arenes enabled by their weak coordination.



Cu(I)-arene complexes with high potentials!

Figure 1. Synthesis of a copper dinitrogen complex supported by the weakly coordinating anion $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) and application as a precursor for homoleptic Cu(I) arene complexes with weakly basic (fluorinated) arenes (xFB, x denotes the number of adjacent fluorine atoms).

References

[1] Willrett, J.; Schmitt, M.; Zhuravlev, V.; Sellin, M.; Malinowski, P. J.; Krossing, I. *Angew. Chem. Int. Ed.*, **2024**, *63*, e202405330. https://doi.org/10.1002/anie.202405330
[2] Armbruster, C.; Sellin, M.; Seiler, M. *et. al. Nat Commun*, **2024**, *15*, 6721.

PARALLEL SESSION II

Organometallic Chemistry

Preparation and Studies of Fluorinated Ligands and their Metal Complexes (Pt, Pd, Zn etc): From Catalysis to the Non-Covalent Bond-Induced C-H and C-C Bond Changes

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The whole series of fluorous pyridines and bipyridines have been synthesized. The high-fluorine content $PtCl_2[5,5'\text{-bis-}(n\text{-}C_{11}F_{23}CH_2OCH_2)\text{-}2,2'\text{-bpy}]$ complex (2) was prepared and employed as recoverable catalyst for the hydrosilylation of alkynes [1]. Pt-catalyst 2 with F-content 0.53 was recovered under the thermomorphic method [2-6] by design and the catalyst was demonstrated capable of re-usage for 8 times without loss of activity. The leaching of Pt in product mixture was monitored, with ICP-MS, to be at as low as 10^{-6} level per cycle in the 5-decyne reactions and at 10^{-3} level per cycle in the $(HO)CMe_2C{\equiv}CH$ reaction. Thus, the easily prepared polyfluorinated (2,2′-bpy)Pt complex 2 is the robust and thermally stable catalyst, which doesn't require specific handling for utilization and storage in laboratory. Additionally, the light-fluorine content $PtCl_2[5,5'\text{-bis-}(ClCF_2(CF_2)_3CH_2OCH_2)\text{-}2,2'\text{-bpy}]$ complex (3) (with F content=31%) was also prepared and employed as recoverable catalyst for the hydrosilylation. It is interesting to find that the ponytail of lightly fluorinated ponytail of $(ClCF_2(CF_2)_3CH_2OCH_2)$- can introduce the good thermomorphic property to the system. Fluorous Pt complex (3)-catalyzed hydrosilation of a variety of silanes with both terminal and internal alkynes was then demonstrated capable of re-usage to furnish the corresponding vinyl silanes in high yields, short reaction times and unique selectivity under thermomorphic conditions. Pt-catalyst 3 with low F-content (31%) easily recovered under the thermomorphic method was found to be an even better catalyst for the hydrosilylation than Pt-catalyst 2. The reaction-catalyst fulfills the principle of green chemistry, and with its addition nature the hydrosilylation delivers 100% atom economy [1-9]. Reported in the latter part is bonding studies. Many new weak interactions involving the fluorous ponytails have been introduced into the fluorous Pt complexes- e.g. $[trans\text{-}(3\text{-}HCF_2CF_2CH_2OCH_2\ py)_2PtCl_2]$. The new weak interactions result in several possible solid state packing of the fluorinated Pt complexes [10-14]. Thus, there are several polymorphs observed for the fluorous Pt complexes with the same chemical formula. It has been also found that this type of fluorous related metal complexes are stable optoelectronic materials which are likely to have good applications in OLED, LED, sensors [15], and solar cells etc. Additionally, the $C\text{-}H\cdots F$ improper hydrogen bonding (HB)[16] and unusual C-H bond elongation and C-C bond change induced by tetrel bond will be discussed [16-18]. The talk will also address how C H bond elongation can be easily offset by forming an improper HB with the H atom of this C–H bond. Non-covalent interactions and electrostatic potential analysis investigations have been used to affirm the nature of the interactions based on density functional theory (DFT), NCI and other related calculations.

References

[1] Lu, N.et al Tetrahedron 2016, 72, 8508-8515. (b) Lu, N.et al Chem. Comm 2011, 47(25), 7227 7229. [2] Bergbreiter, D. E.; Sung, S. D. Adv. Synth. Catal. 2006, 348, 1352–1366. [3] Bergbreiter, D. E. et al J. Am. Chem. Soc. 2000, 122, 9058 9064. [4] Dioumaev, V. K.; Bullock, R. M. Nature 2003, 424, 530–532. [5] Wende, M.; Meier, R.; Gladysz, J. A. J. Am. Chem. Soc. 2001, 123, 11490-11491. [6] Wende, M.; Gladysz, J. A. J. Am. Chem. Soc. 2003, 125, 5861-5872. [7] Zhou, Q. C. H. et al Science 2014, 345, 542–546. [8] (a) Connick, W.B. et al Inorg. Chem., 1996, 35, 6261 6265. [9] (a) Shing, J.S. et al Inorg. Chem 2011, 50(10), 4289-4294. (b) Lu, N. et al Dalton Trans. 2014, 43, 2112–2119. [10] Kong, P.-C.; Rochon, F. D. Can. J. Chem, 1978, 56(4), pp 441-445 [11] Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements, 2nd Ed.; Oxford: Butterworth Heinemann, 1997. [12] Lu, N. et al Acta Cryst. C, 2017, 73, 343 349. [13] Connick, W. B. et al Inorg. Chem., 1997, 36, 913–922. [14] Lu, N. et al J. Fluorine Chem, 2018, 206, 29-35. [15] Lu, N.; et al ACS Applied Materials & Interfaces 2025, 17 (1), 1743-1759. [16] Lu*, N. et al J. Am. Chem. Soc. 2021, 143, 14, 5550–5557. [17] Elakkat, V. et al Chem. Comm. 55 (95), 14259-14262. [18] V. Elakkat, et al Angew. Chem. Int. Ed. 2023, 62, 6, e202215438.

Novel $Cu^{III}CF_3$ Compounds Relevant to C−C and C−Heteroatom Bond Formation

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Fluorine atoms drastically affect the biological properties of organic synthons,[1] with the trifluoromethyl group occupying a preferential place in drug and agrochemical design. The creation of C–CF_3 bonds *via* cross-coupling reactions thus represents an appealing strategy to build molecular complexity, but unfortunately, the C–CF_3 bond formation *via* reductive elimination (R.E.) from [R–TM–CF_3] fragments represents a challenging task. An original approach to circumvent this bottleneck resides in the building of high-valent [R–TM–CF_3] organometallic platforms, which are more prone to get reduced, thereby making the key R.E. step easier (**Figure 1**). In this communication, an expeditious entry to unprecedented high oxidation state $Cu^{III}CF_3$ compounds together with their application in trifluoromethylation[2] and C–heteroatom[3] bond formation will be disseminated.[2-3] More precisely, the authentication of $Cu^{III}CF_3$ species, alongside their crucial role in trifluoromethylation reactions *via* uncommon $2e^-$ redox shuttles, will be presented.

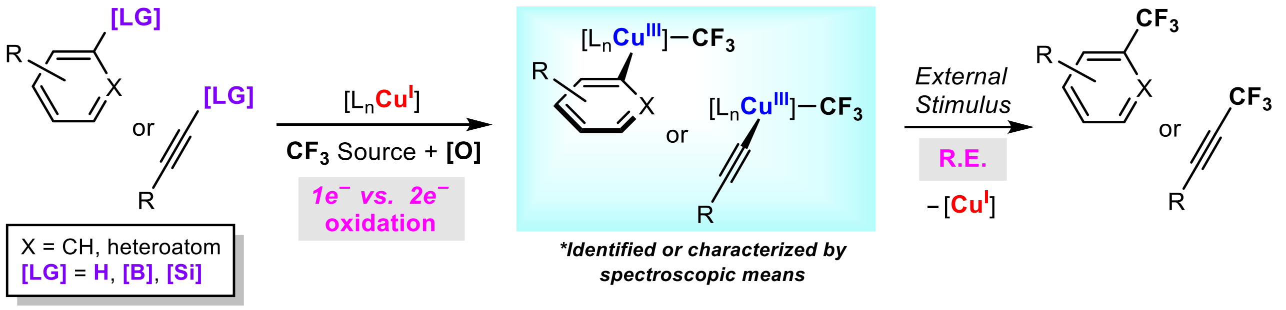

Figure 1. Guiding principle of this talk: Synthesis of high oxidation state $Cu^{III}CF_3$ complexes *via* $2e^-$ oxidation step and subsequent use for synthetic purposes (trifluoromethylation).

References

[1] K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881. (b) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470.
[2] N. Nebra, V. V. Grushin, *J. Am. Chem. Soc.* **2014**, *136*, 16998. (b) A. M. Romine, N. Nebra, A. I. Konovalov, E. Martin, J. Benet-Buchholz, V. V. Grushin, *Angew. Chem., Int. Ed.* **2015**, *54*, 2745. (c) D. Joven-Sancho, A. Echeverri, N. Saffon-Merceron, J. Contreras-Garcia, N. Nebra, *Angew. Chem., Int. Ed.* **2024**, 63, e202319412.
[3] L. Antonini, J. Joly, L. Demonti, D. Joven-Sancho, N. Saffon-Merceron, A. Caselli, N. Nebra, *manuscript in preparation*.

Using *ortho*carborane as a replacement for the aryl group to greatly increase the oxidizing power of “$ArIF_2$” and “$ArI(OTf)_2$”

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Hypervalent I(III) reagents are widely used as oxidizing agents for organic and inorganic transformations. The most common scaffold for these is based on $ArIL_2$, where Ar is an aryl group and L is a ligand. If the aryl group or ligand is more electron poor/less nucleophilic the oxidative potential of the iodine is increased. Fluorine is thus very important in both aspects, due to the electron withdrawing nature of fluorine, and the typically poor nucleophilicity of ligands with a high fluorine loading (eg triflate). If the iodine in $ArIL_2$ becomes too electron poor, decomposition via electrophilic aromatic substitution becomes a problem, and $ArI(OTf)_2$ represents the limit for how electron poor these can be. In this presentation we will discuss how electron withdrawing *ortho*-carborane ligands can be used to replace the aryl group and describe the first $oCbIL_2$ type compounds for L = -F and -OTf. Preliminary results suggest these compounds are much more powerful oxidizing agents than the traditionally used $ArIL_2$ compounds.

Transition Metal Interconversion of Semi and Perfluoroalkyl Halides

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The special properties promoted by the presence of C-F bonds have enabled semi- and perfluorinated compounds (*e.g.* haloperfluorohalides, R-CF_2-X, X = Cl, Br, I etc.), to permeate all fields of chemistry including organic, pharma and polymer, and sustain a vigorous and ever-growing field of research.

However, the syntheses of commercial R_F-X (available with Cl >> Br >> I, but preferred with X = I based on reactivity), each follow divergent procedures which are expensive, toxic and require very drastic conditions. In addition, the *direct* interconversion of the primary R_F-CF_2-X to R_F-CF_2-Y is extremely difficult due to the strong deactivating effect of the fluorine which effectively blocks nucleophilic substitutions. Thus, no simple, direct, efficient and convenient halide interconversion procedure is currently available. As such, the development of novel chemistry for the activation of strong CF_2-X (X = Cl, Br etc.), bonds and for perfluoroalkyl halide interchange or further derivatization, is highly desirable and would greatly expand the toolbox and applications of fluorine chemistry.

We are presenting herein the development of an inexpensive, mild, efficient, safe, fast and *catalytic* transition metal mediated universal interconversion of R_F-X to R_F-Y (X, Y = F, Cl, Br, I, N_3, etc.) derivatives, the study of the reaction mechanism, and rational selection of the reaction parameters (metal, ligand, substrate structure, temperature, solvent etc.).

Enhancing Pd(IV) Stability: Trifluoromethyl Organopalladium Complexes

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In the past 50 years, palladium reagents and catalysts have been widely used in organic and organometallic chemistry owing to their exceptional ability to promote a broad range of useful organic transformations.[1] The involvement in such processes of organopalladium species in high oxidation states has been recognized only in the last decades though.[2] Many organometallic Pd(IV) compounds have been ever since reported and their reductive elimination pathways extensively studied. It must be noted, however, that the stabilization of organopalladium(IV) compounds typically requires the assistance of at least one chelating ligand.[3]

The trifluoromethyl group, CF_3, excels at stabilizing high oxidation states in transition metal complexes.[4] Given its remarkable group electronegativity,[4] it might well be a suitable ligand to stabilize Pd(IV) without the need for ancillary chelating ligands. Building on our extensive experience with CF_3 transition metal complexes in high oxidation states (Pt, Au, Ag),[5] we sought to apply similar strategies to Pd.

In this work, we present a novel series of organopalladium(IV) compounds stabilized by CF_3 ligands. They are prepared by oxidative addition of halogens to the homoleptic Pd(II) complex $[PPh_4]_2[Pd(CF_3)_4]$. Experimental methods have been devised to selectively obtain the *cis* and *trans* isomers (Figure 1). Both the *cis* and *trans* isomers undergo further ligand substitution with other nucleophiles, with retention of the stereochemistry. All the obtained compounds are rare cases of organopalladium(IV) complexes bearing no chelating ligand.

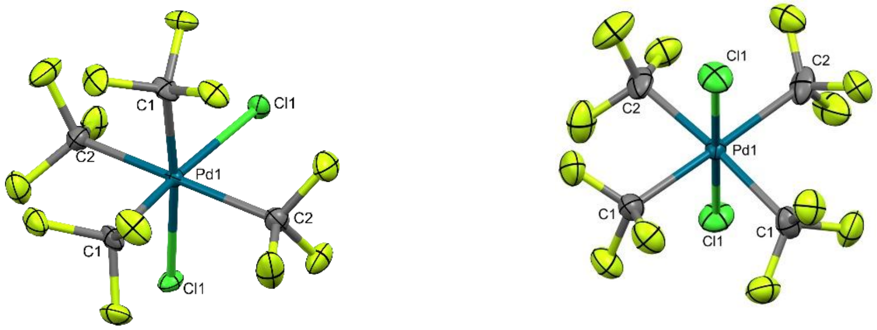

Figure 1. XRD structures of the *cis* and *trans* isomers of the $[Pd(CF_3)_4Cl_2]^{2-}$ anion.

References

[1] Tsuji, J. *Palladium Reagents and Catalysts*, Wiley **2004**.
[2] Muñiz, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9412–9423.
[3] Vedernikov, A.N. in *Comprehensive Organometallic Chemistry IV, Vol. 8*; Elsevier **2022**, pp. 783–835.
[4] García−Monforte, M.A.; Martínez−Salvador, S.; Menjón, B. *Eur. J. Inorg. Chem*. **2012**, 4945–4966
[5] a) Joven−Sancho, D.; Baya, M.; Falvello, L.R.; Martín, A.; Orduna, J.; Menjón, B. *Chem. Eur. J.* **2021**, *27*, 12796–12806. b) Menjón, B.; Martínez−Salvador, S.; Gómez−Saso, M.A.; Forniés, J.; Falvello, L.R.; Martín, A.; Tsipsis, A. *Chem. Eur. J.* **2009**, 15, 6371–6382

Investigation of CAAC Stabilized Niobium and Tantalum Pentafluorides

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High valent niobium and tantalum pentahalides have received much attention in recent decades due to the easy availability of the compounds and their non-toxicity. Interest in these compounds also grew due to their potential applications in materials chemistry, organic synthesis or as precursors of weakly coordinating anions [1]. In addition, the functionalized Nb(V) and Ta(V) compounds, in which halide substituents are exchanged for other functional groups, have found interesting applications in catalysis, making them desirable compounds to explore [1].

In the past, our group has focused on the carbene chemistry of NbF_5 and TaF_5. In 2016, we succeeded in the preparation and structural characterization of the first NHC-stabilized NbF_5 and TaF_5 complexes as well as their $[NbF_6]^-$ and $[TaF_6]^-$ salts [2]. These results have inspired us to extend our research to another group of carbene ligands, the cyclic(alkyl)(amino) carbenes (CAACs), whose chemistry has not yet been tested on group V fluorides.

In this contribution, our recent work on the chemistry of NbF_5 and TaF_5 with CAACs will be presented and compared with the structurally related NHCs. The sterically less demanding CAAC carbene has the ability to form neutral dimer units upon complex formation, which possess a 7-coordinate pentagonal bipyramidal geometry at the metal center (Figure 1).

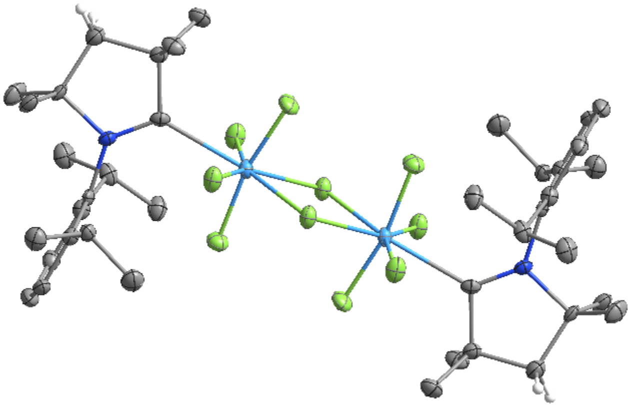

Figure 1. Crystal structure of the dimeric $[(^{Me}CAAC)TaF_5]_2$.

References

[1] Bresciani, G.; Bortoluzzi, M.; Zacchini, S; Marchetti, F.; Pampaloni, G. *Eur. J. Inorg. Chem.*, **2018**, *2018 (8)*, 999-1006.

[2] Zupanek, Ž; Tramšek, M; Kokalj, A; Tavčar, G. *J. Fluor. Chem.*, **2019**, *227*, 109373.

Homoleptic Platinum(IV)–CF_3 and –$OTeF_5$ Complexes as Potential Precursors for Platinum Species in Higher Oxidation States

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Homoleptic transition metal complexes are prototypical species in the development of coordination and organometallic chemistry due to their simple nature.[1] In the particular case of homoleptic d-block metal –CF_3 and –$OTeF_5$ complexes, only a few representatives are known for Group 10-12 metals, with oxidation states ranging from +I to +III. Even more scarce are six-coordinate homoleptic –CF_3 and –$OTeF_5$ complexes, which are virtually unknown for late transition metals. In fact, for the –CF_3 ligand, only the synthesis of $W(CF_3)_6$ and $U(CF_3)_6$ in a C_2F_6 plasma has been reported,[2] whereas for the –$OTeF_5$ group, only a few species containing early d-block metals (Groups 4-6) are known.[3,4]

Herein, we present the multi-step synthesis of $[Pt(CF_3)_6]^{2-}$, the first structurally characterized d-block metal complex bearing six trifluoromethyl ligands. The synthesis starts from the highly trifluoromethylated precursor $[Pt(CF_3)_5I]^{2-}$,[5] with the final step involving fluorination of a cyanido ligand in a ClF/KF system (Figure 1). Additionally, we demonstrate a one-step synthesis of $[Pt(OTeF_5)_6]^{2-}$ using the strong oxidizer $ClOTeF_5$, yielding the first late d-block metal pentafluoroorthotellurate complex with an oxidation state higher than +III. Both complexes are fully characterized and the oxidation of the platinum(IV) center is investigated.

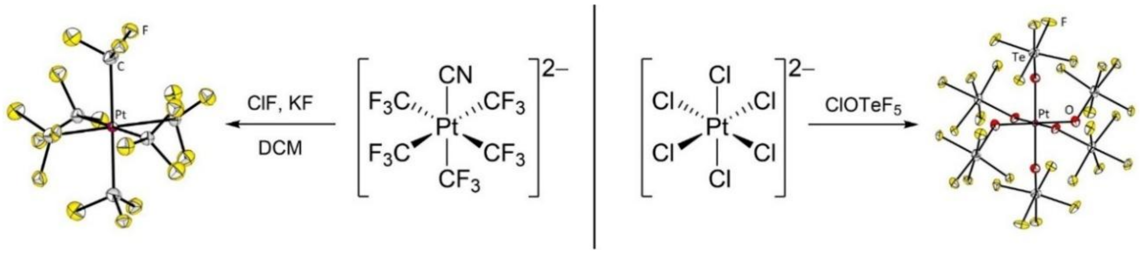

Figure 1. Syntheses and molecular structures in the solid state of the homoleptic platinum(IV) complexes $[Pt(CF_3)_6]^{2-}$ and $[Pt(OTeF_5)_6]^{2-}$.

References

[1] Alvarez, S.; Cirera, J. *Angew. Chem. Int. Ed.*, **2006**, *45 (19)*, 3012-3020.
[2] Lagow, R. J. *Synthesis of volatile uranium compounds*, Report, Massachusetts Institute of Technology, **1977**.
[3] Seppelt, K. *Angew. Chem. Int. Ed.*, **1982**, *21 (12)*, 877-956.
[4] Gerken, M.; Mercier, H. P. A.; Schrobilgen, G. J. in *Advanced Inorganic Fluorides* (Eds.: Nakajima, T.; Zemva, B.; Tressaud, A.), Elsevier, Lausanne, **2000**, pp. 117-174.
[5] Martínez-Salvador, S.; Forniés, J.; Martín, A.; Menjón, B. *Chem Eur. J.* **2011**, *17 (29)*, 8085-8097.

PARALLEL SESSION II

Contaminants of Emerging Concern and Fluorous Technology (sponsored by F-GASES)

Development and Scale-up of Thin Film Polymer Membranes for the Separation and Recycling of Fluorinated Refrigerants

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The rising demand for refrigeration and air conditioning and the stringent regulations on the production of high global warming potential (GWP) hydrofluorocarbons (HFCs) are boosting the development of innovative separation processes aimed at increasing the global share of recycled HFCs. Among the various advanced separation techniques being assessed, membrane technology can play a significant role in designing energy-efficient separations for the recovery of the most valuable compounds, such as difluoromethane (R-32), from refrigerant blends recovered from end-of-life equipment (e.g., R-410A, R-454B and R-407C). However, the industrial implementation of membrane units not only requires very selective barrier materials, but also the successful development of compact membrane devices incorporating thin-film selective layers, which is seldom addressed. Thus, in this work, we will show the steps given by our research group from the design and selection of the most promising polymers for the selective separation of HFCs, to the fabrication of defect-free thin film composite membranes in hollow fiber configuration (HF-TFCMs) and characterization of their gas permeation properties for the most common HFCs and novel hydrofluoroolefins (HFOs). The HF-TFCMs were fabricated with advanced polymers, including different types of fluorinated aromatic polyimides (F-PI) as well as polymers of intrinsic microporosity (PIM-1) with different degrees of branching [1]. Then, the polymer that exhibited the best results in terms of permeability, selectivity and long-term performance was selected for the production of HF-TFCMs. The lab scale HF-TFCMs were prepared by dip coating the F-PI 6FDA-TMPD over a PDMS-impregnated polypropylene HF porous support. These membranes showed an excellent performance for the separation of R-32 with purity above 99 vol% from the binary refrigerant mixtures R-410A and R-454B, and great potential for the recovery of R-32 from the ternary blend R-407C [2]. Finally, further steps forward have been given through the fabrication and testing of a larger scale membrane module containing homogeneous 6FDA-TMPD HFs and testing of a membrane pilot plant located in a waste management facility of devices containing F-gases.

Acknowledgements

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References

[1] S.V. Gutiérrez-Hernández, F. Pardo, A.B. Foster, P. Gorgojo, P.M. Budd, G. Zarca, A. Urtiaga, *J. Membr. Sci.*, **2023**, 675, 121532.

[2] S.V. Gutiérrez-Hernández, S. Rico-Martinez, F. Pardo, C. Álvarez, J.A. Miguel, G. Zarca, A. Urtiaga, *J. Membr. Sci.*, **2024,** 698, 122617.

Capture and Separation of Fluorinated Gases with High.Global Warming.Potential

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Fluorinated gases (F-gases) are a family of synthetic gases used in a large range of industrial applications, being used as substitutes for ozone-depleting substances. These compounds are powerful greenhouse gases (GHG) with global warming effects up to 23000 times greater than carbon dioxide. In the EU, their emissions have increased up to 60% since 1990 in contrast to all other GHG whose emissions have been reduced. The development of technologies for efficient reclamation of F-gases is relevant, not only to reduce GHG emissions to the atmosphere, but also because of their market value. For the separation and capture of F-gases, porous solid matrices (activated carbons (ACs), metal–organic frameworks (MOFs) and zeolites) have been used to avoid the release of F-gases into the atmosphere.[1,2] Furthermore, the Acs are commercially available and possess attractive structural characteristics that allow them to be used as very efficient adsorbents in industrial processes.[3] This work aims to reduce the environmental impact of the most used F-gases in air conditioning and commercial refrigeration, such as, difluoromethane (R-32), 1,1,1,2-tetrafluoromethane (R-134a), pentafluoroethane (R-125) and 1,1,1-trifluoroethane (R-143a). Then, BPL-activated carbon was used to measure the adsorption equilibria with all F-gases at 283.15, 303.15K and 323.15K. In addition, the adsorption equilibrium and kinetics of pure gases was also studied. Several breakthrough experiments were performed to determine the dynamic behaviour and validate a mathematical model for process design using simulation tools. This work demonstrated a promising and attractive solution for the capture of F-gases using BPL-activated carbons.

References

(1) Schulz, M.; Kourkoulas, D. Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on Fluorinated Greenhouse Gases and Repealing Regulation (EC) No 842/2006. Official Journal of the European Union 2014, 2014 (517), L150/195-230.
(2) Sosa, J. E.; Ribeiro, R. P. P. L.; Matos, I.; Bernardo, M.; Fonseca, I. M.; Mota, J. P. B.; Araújo, J. M. M.; Pereiro, A. B. Exploring the Potential of Biomass-Derived Carbons for the Separation of Fluorinated Gases with High Global Warming Potential. Biomass Bioenergy 2024, 188, 107323. https://doi.org/https://doi.org/10.1016/j.biombioe.2024.107323.
(3) Sosa, J. E. J. E.; Malheiro, C.; Ribeiro, R. P. P. L. R. P. P. L.; Castro, P. J. P. J.; Piñeiro, M. M. M. M.; Araújo, J. M. M. J. M. M.; Plantier, F.; Mota, J. P. B. J. P. B.; Pereiro, A. B. A. B. Adsorption of Fluorinated Greenhouse Gases on Activated Carbons: Evaluation of Their Potential for Gas Separation. Journal of Chemical Technology and Biotechnology 2020. https://doi.org/10.1002/jctb.6371.

An Innovative Hybrid Membrane-Adsorption (HAMSYS) Technology for The Selective Recovery of F-gases from Depleted Refrigerant Blends

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Fluorinated gases (f-gases) possess an exceptionally high global warming potential (up to 23,500 times CO_2), emphasizing the urgent need to mitigate the emissions from sectors such as refrigeration and air-conditioning (RAC), one of the main contributors to climate change. In addition, within the framework of European climate change regulations, the phasedown of specific f-gases has further underscored the necessity of formulating new blends that align with both environmental goals and regulatory requirements.

In this context, the LIFE-4-Fgases project seeks to design and develop cutting-edge hybrid technology to enable the selective recovery of specific individual f-gases from depleted commercial refrigerant blends, facilitating their reuse in the formulation of new, environmentally friendly alternatives. The design has been based on both experimental results at a laboratory scale and the use of advanced simulation tools, developing a highly versatile system capable of working with both binary and ternary mixtures. The so called HAMSYS (Hybrid Adsorption and Membrane Systems) integrates the following: i) A pretreatment unit including coalescing filtration to purify f-gases; ii) a two-step separation process, which integrates a polyimide membrane unit followed by an adsorption system that uses activated carbon to preferentially adsorb the target compounds and iii) a compressor to prepare the f-gases for storage and transportation.

Figure 1. Image of the front view of the HAMSYS prototype.

By the preliminary experimental results carried out using depleted R410A (i.e. R32:R125 1:1), HAMSYS has reached important R32 recovery rates, with the purity requested by ARHI standard. Therefore, it is demonstrated the potential of this technology to foster the implementation of circular economy principles withing the RAC sector, reducing waste, maximizing resource efficiency and mitigating climate change.

LIFE-4-Fgases: Dissemination and Communication Activities

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The LIFE 4-FGases project, successor to the KET4F-GAS project, aims to help improve the sustainability of the refrigeration and air conditioning sector by developing a prototype to demonstrate the feasibility of efficiently separating high global warming potential (GWP) HFCs from refrigerant mixtures contained in end-of-life refrigeration equipment. An innovative Hybrid Adsorption Membrane System (HAMSYS) for the selective recycling of HFC blends has therefore been developed, which can be applied in the facilities of Waste Management Operators that treat this type of waste. With this system, the separated substances can then be used to formulate new refrigerant mixtures that are more environmentally friendly and have a lower global warming potential (GWP), thereby minimizing the environmental impact of this sector. As part of the European Recycling Platform, the first pan European platform of Electrical and Electronic Waste (WEEE) management, ERP Portugal is a private law non-for-profit association operating as a WEEE Compliance Scheme since 2006. The expertise acquired by ERP across Europe, allows it to have a deep knowledge of the sector that goes from the electric and electronic equipment placed on the market to its final destination, i.e., e-waste' recycling, recovery and preparation for reuse. This gives ERP PT an important role in promoting this project to the key stakeholders involved in the life cycle of refrigeration equipment containing fluorinated gases, particularly recyclers and installing companies.Thus, in its first year, the project was promoted among European WEE PRO through the Landbell Group's communication lines. The aim was also to gather contacts of European Recyclers so that they could answer a survey regarding F-Gas recycling, prepared by the project's partners, to sustain a benchmark of the main solutions implemented across Europe. Through this action, 58 entities were contacted by email, with 14 EU countries covered.

In 2023, as part of the European Week for Waste Reduction, ERP PT promoted a Cycle of Talks: ''Separar é o que nos une'', dedicating an exclusive webinar to the LIFE 4F-gases project. The issue of fluorinated gas emissions was addressed, showing the potential impact of the HAMSYS technology in the WEEE recycling sector. The event was attended by various stakeholders, with a total of 27 participants, including representatives of public bodies (i.e., Portuguese Environment Agency), as well as producers of air conditioning equipment and recyclers related to the fluorinated gases sector. Last year, it was developed a set of materials to communicate and disseminate the project, consisting of two videos, a flyer, a tryptic and social media posts. This communication materials were presented in several activities that ERP PT organised with its partners in the education sector, under the Geração Depositrão project, which is a partnership with the Portuguese Eco-schools Program, from European Blue Flag Association, that covers students of all ages and focus on four main aspects: WEEE and batteries collection, creative activities, awareness-raising sessions and quizzes on the concept of "Sustainability", with a special focus on WEEE management. This action reached 2 174 schools.As the project draws to a close, the communication plan is reaching its highest point, with a reinforcement of the actions to be carried out, making it possible to publicize the results obtained. To this end, various dissemination activities are planned for 2025, such as stepping up communication on the media and publishing an article about the project in specialized journals related to environment, chemistry, sustainability and innovation topics.

An Innovative Technology for The Selective Recovery of F-gases from Depleted Refrigerant Blends

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Fluorinated gas emissions, mainly employed in the refrigeration and air conditioning sector, are one of the main contributors to climate change. These emissions have increased 60% since 1990.
Nowadays, due to the lack of available technology, most of the depleted fluorinated gases employed as refrigerants are treated as residues and incinerated.

The objective of the LIFE-4_FGASES Project is to demonstrate an innovative technology that allows the selective recovery of the fluorinated gases present in commercial refrigerant blends and, therefore, their reutilization, minimizing their environmental impact, and to implement the principles of circular economy at industrial level.
The innovative hybrid system developed for LIFE-4-FGASES, called HAMSYS (Hybrid Adsorption and Membrane Systems), integrates membrane technology and adsorption processes.

AMBIGROUP RECICLAGEM SA is a company that belongs to AMBIGROUP SGPS group, which has been operating in the market for over 40 years, having started its activity in scrap metal recycling.
Today its workforce exceeds 500 employees in 8 recycling plants spread across the north and south of Portugal, offering an integrated waste management and recycling solution.
AMBIGROUP RECICLAGEM SA is a company dedicated to recycling metals, electrical and electronic waste, plastics, end-of-life vehicles and metal packaging. In our recycling unit we operate with the best technologies available to make the Circular Economy a reality.
AMBIGROUP RECICLAGEM SA is licensed as a waste management operator, and it is the only company in Portugal with WEEELABEX certification, regarding Waste Electrical and Electronic Equipment Treatment process with the requirements of the European Standards and Technical Specifications approved by the European Electrotechnical Committee for Standardization (CENELEC), for Temperature exchange equipment's: Manual and Mechanical treatment.
This accreditation certifies compliance with CENELEC standards for the treatment of refrigeration equipment.
The WEEELABEX benchmark (specific international standards for WEEE) reflects excellence in the treatment of WEEE at European level.
As a company focused on continuous process improvement and the search for new and better technologies to solve environmental problems, AMBIGROUP RECICLAGEM SA immediately agreed to be a partner in this project.
Having contributed to the project with technical knowledge and experience of working effectively in the recycling of temperature regulating equipment, carrying out the correct decontamination/depollution, treatment/recovery of all the fractions resulting from this process.

PARALLEL SESSION III

Organic Chemistry

Expanding SF_5 Chemistry

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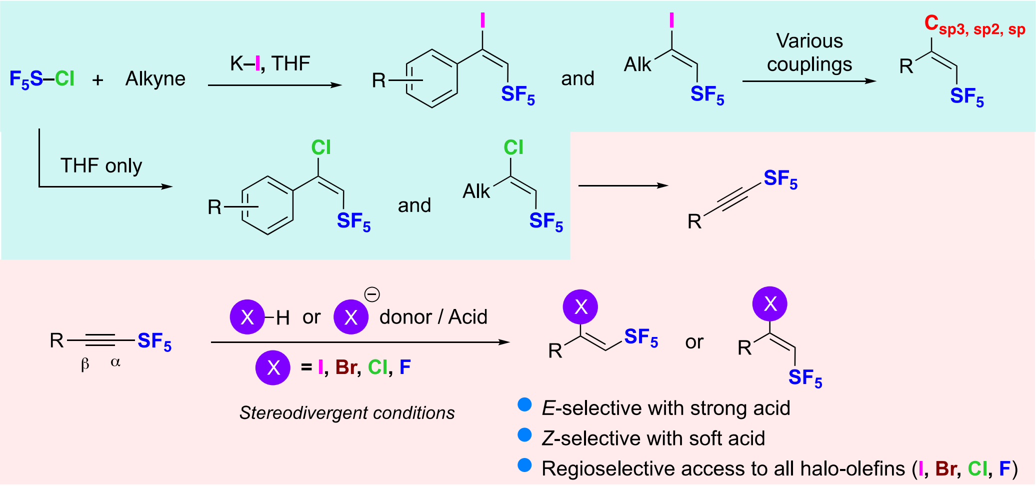
The sulfur pentafluoride SF_5 group is one of the rare functional groups in the present-day investigation allowing to broaden out our perspective in organic chemistry. Outstanding physico-chemical properties, unique spatial charge distribution and potential uses in the next generation of fluorochemicals justify the current strong interest. The development of SF_5-substituted aliphatic compounds remains underexplored compared to SF_5-substituted aromatic compounds. In this symposium, I will present simple approaches to access know and novel SF_5 compounds. Firstly, we focused on tracking the *de novo* SF_5I reagent and exploring its reactivity.[1] We formally succeeded in taming this hitherto unknown reagent. Design experiments and computational DFT studies suggest a radical iodopentafluorosulfanylation mechanism, albeit with *in situ* formation of SF_5^- anion. Next, we identified a robust protocol enabling SF_5Cl addition to alkynes, providing a variety of established and unprecedented chloropentafluorosulfanyl alkenes, using simply the solution of SF_5Cl in THF.[2] Finally, we explored the ambiphilic reactivity of SF_5-alkynes and proved that they can act as both nucleophiles and electrophiles. We developed highly selective stereodivergent hydrohalogenation (I, Br, Cl, F) reactions of SF_5-alkynes.[3]



Scheme 1. Pentafluorosulfanylation of alkynes and subsequent transformations.

References

[1] T.M. Nguyen, C.Y. Legault, N. Blanchard, V. Bizet, D. Cahard. *Chem. Eur. J.* **2023**, *29*, e2023029.

[2] T.M. Nguyen, L. Popek, D. Matchavariani, N. Blanchard, V. Bizet, D. Cahard. *Org. Lett.* **2024**, *26,* 365-369.

[3] D. Matchavariani, L. Popek, J J. Cabrera-Trujillo, T M. Nguyen, N. Blanchard, K. Miqueu, D. Cahard, V. Bizet. *Adv. Synth. Catal*. **2024**, *366*, 3481–3493.

Collection of Quality-Evaluated pKa Values in Polar Aprotic Solvents

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This presentation is about a compilation of pK_a values of close to 5000 acids (among them more than 500 fluorocompounds) containing more than 9000 pK_a values determined in seven dipolar non-hydrogen-bond-donor solvents (dimethyl sulfoxide, acetonitrile, N,N-dimethylformamide, pyridine, acetone, propylene carbonate, tetrahydrofuran) collected from around 800 original works published during the last eighty years. The data have been critically evaluated on the basis of defined quality criteria and depending on situation, kept as they were originally published, marked as doubtful/unreliable (around 2700 values) or corrected (around 2500 values). The work was carried out in the framework of the IUPAC project 2015-020-2-500 (https://iupac.org/project/2015-020-2-500/).

The first version of the data compilation has been finalised and is available at https://doi.org/10.5281/zenodo.12608876. To enable automated processing and mining, the data are presented as a set of spreadsheets, together with structural codes (SMILES and InChI strings), compound class qualifiers and comments. It is a "living" database, i.e. the authors will continue working with it – correcting possible mistakes and adding new data. The above Zenodo link will always point to the most recent version. At the time of preparing this abstract the accompanying publication in *Pure and Applied Chemistry* [1] is in the last stage of reviewing. By the time of the 21st ESFC conference it will most likely be published.

The presentation will give an overview of the data, the descriptors, how the data were quality-evaluated and corrected when needed.

References

[1] Leito, I.; Kaljurand, I.; Piirsalu, M.; Tshepelevitsh, S.; Zheng, J.; Roses, M.; Gal, J.-F. Acid Dissociation Constants in Selected Dipolar Non-Hydrogen-Bond-Donor Solvents (IUPAC Technical Report). *Pure and Applied Chemistry* **2025**, Under revision.

3,3-Difluoroallyl Sulfonium Salts: Practical and Bench-Stable Reagents for Highly Regioselective *gem*-Difluoroallylations

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A novel, practical, bench-stable, and highly active *gem*-difluoroallylating reagent, 3,3-difluoroallyl sulfonium salt (DFAS), using the inexpensive industrial chemical 3,3,3-trifluoropropene (TFP) as the starting material has been developed.[1,2] This reagent can be applied to the construction of a series of C(sp^3)-CF_2R bonds, with excellent regioselectivity and functional group tolerance, and it can also be used in catalytic asymmetric synthesis.[3] Moreover, this reagent can be employed for bioorthogonal fluorination of peptides and proteins,[4,5] thus providing an effective tool for peptide and protein engineering and chemical biology.

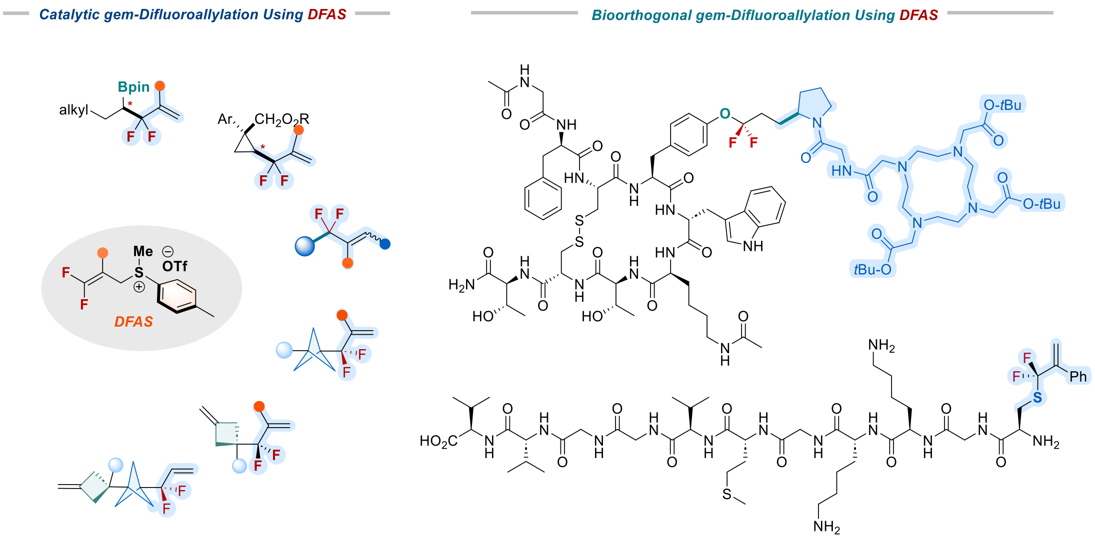

Figure 1. Highly selective *gem*-difluoroallylation with DFAS

References

[1] Feng, X.-T.; Ren, J.-X.; Gao, X.; Min, Q.-Q.; Zhang, X. *Angew. Chem. Int. Ed.* **2022**, *61*, e202210103.
[2] Feng, X.-T.; Min, Q.-Q.; Zeng, X.; Zhao, H.-Y.; Zhang, X. *ACS Catal.* **2024**, *14*, 5879.
[3] Gao, X.; Ren, X.; Deng, W.; Zhang, X. *Chin. J. Chem.* **2023**, *41*, 3521.
[4] Ren, J.-X.; Zhou, M.; Feng, X.-T.; Zhao, H.-Y.; Fu, X.-P.; Zhang, X. *Chem. Sci.* **2024**, *15*, 10002.
[5] Zhou, M.; Ren, J.-X.; Feng, X.-T.; Zhao, H.-Y.; Fu, X.-P.; Min, Q.-Q.; Zhang, X. *Chem. Sci.* **2024**, *15*, 2937.

Liquid-crystalline Properties Induced by Incorporating Fluorines into D-π-A Tolane Containing Decyleneoxy Chains Terminated with Imidazolium Salts

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Liquid crystals (LCs) are a mesophase between an optically anisotropic crystal with molecular orientation and positional order and an optically isotropic liquid without molecular orientation and positional order. These materials have attracted considerable attention as soft materials for applications, such as light-driven smart windows, stimulus-responsive actuators, and biosensors. Numerous LC molecules have been developed, and among the existing LC molecules, compounds with a diphenylacetylene skeleton are well known as rod-shaped π-conjugated mesogens. Recently, our group has developed fluorescent LCs that possess both fluorescent and LC properties. Our previous studies have shown that donor-π-acceptor (D-π-A) tolane derivatives can serve as fluorescent π-conjugated mesogens, which has potential applications in thermosensing PL materials.

Based on our previous studies, to elucidate the effect of fluorine introduced into D-π-A tolane-type mesogens, non-fluorinated tolanes **1-X** and tetrafluorinated analogues **2-X** with imidazolium-terminated flexible chains with different counter anions (**X**) were synthesized and their phase transition behavior was investigated (Figure 1).

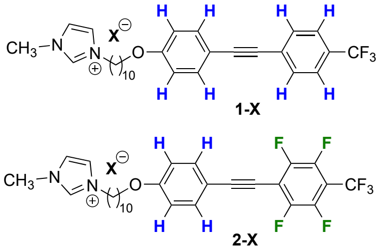

Figure 1. Chemical structures for compounds **1-X** and **2-X** used in this study.

Compounds **1-Br** with a Br⁻ ion or **1-NTf₂** with a NTf_2^- ion as counter anions of the imidazolium salt showed a smectic A (SmA) and a nematic (N) phase in a narrow temperature range, while derivatives with PF_6^- ion or OTf⁻ ion showed no mesophase (Figure 2a). In contrast, in the case of tetrafluorinated analogues, the formation of a layered SmA phase and a highly ordered unidentified Sm phase was observed in almost all compounds, regardless of the counter anion (Figure 2b). These results indicates that the introduction of fluoro-substituents into the mesogens led to reduced crystallinity, contributing to the expression of the LC phase.

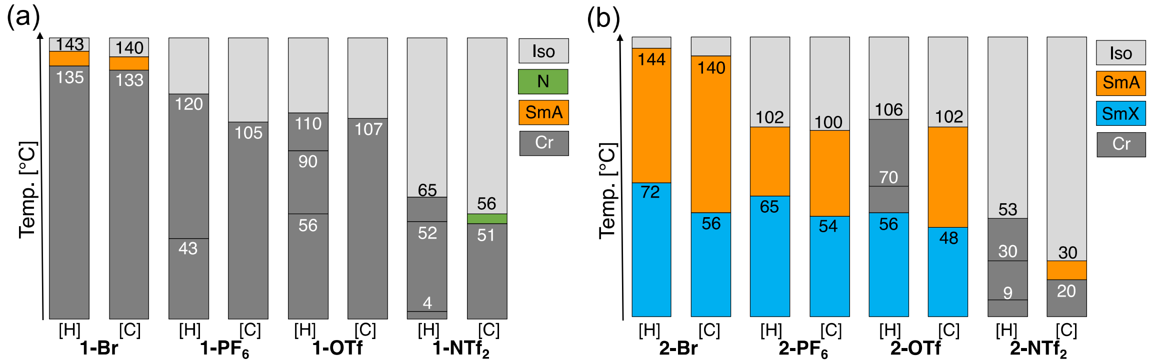

Figure 2. A bar graphs illustrating phase sequence and transition temperature [°C] of (a) **1-X** and (b) **2-X** series during the second heating and cooling processes. Notation: Cr, crystalline; SmX, unidentified smectic; SmA, smectic A; N, nematic; Iso, isotropic phase.

Simple and Efficient Approach to Sulfonyl Fluorides

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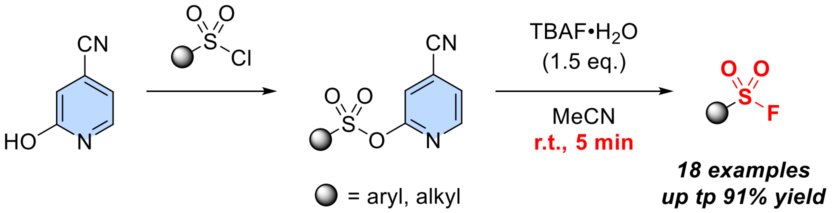
Sulfonyl fluoride (SO_2F) has attracted a widespread attention since sulfur-fluoride exchange (SuFEx) was introduced in 2014. Existing SO_2F synthesis methods are facing challenges in the use of toxic gases and generation of hydrogen fluoride. Here, we report a simple, efficient method for building SO_2F using 4-cyanopyridone as a leaving group. This reaction takes place quickly in five minutes with diverse substrates, including aromatic, aliphatic, and sterically hindered compounds, as well as ester, amide, and heteroatoms, overcoming limitation of traditional methods.



- **Easily isolation and purification**
- **No use of toxic gases**
- **5 minute reaction**

PARALLEL SESSION III

Materials and Fluorous Technology

Key Aspects in Corrosion of Superalloys in Molten Fluoride Salts

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The main identified aspect in the corrosion of Incoloy 800H/HT in molten FLiNaK (eutectic mixture of LiF, NaF and KF) is the fact that hydrogen, in the form of HF and/or H_2O, contributes to the corrosion acceleration dramatically (up to six-fold) in comparison with the only oxygen presence. This observation was confirmed on the series of selected additives (CrF_3, $CrF_3.3H_2O$, Cr_2O_3, Na_2O, KF, and KHF_2). The role of additives was to serve as so-called corrosion accelerators in order to speed up the corrosion process of the material. The authors performed accelerated corrosion tests to confirm previous findings [1, 2, 3] and at the same time to resolve inconsistencies found in the literature. From the point of view of the corrosion efficiency of the FLiNaK eutectic mixture on the Incoloy 800H/HT model alloy, not only the effect of additions but also their concentration of the listed salts containing chromium, oxygen, hydrogen or water was evaluated. In addition, two different crucible materials were used, sintered alumina and glassy carbon. Corrosion strength of investigated additives increases in order Na_2O < KF < Cr_2O_3 < CrF_3 < KF.HF < $CrF_3.3H_2O$. These findings were supported by the following techniques. Extensive corrosion attack was observed on the surfaces of all samples, and SEM-EDX cross-section analysis revealed selective dissolution of elements, primarily chromium and iron. Gravimetric analysis demonstrated that weight changes were highly dependent on the specific salt mixture used, particularly the concentration of added salts. Corrosion rate was found to be higher when glassy carbon crucibles were used, owing to galvanic corrosion. In summary, the corrosion rate can be augmented by employing acidic or hydrated salts, selecting a specific crucible material, and adjusting the concentration and type of additives utilized.

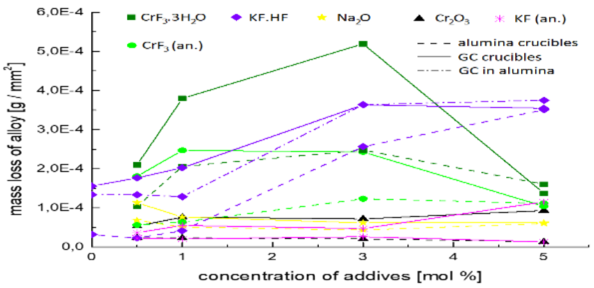

Figure 1. Dark green squares = hydrated CrF_3, light green circles = anhydrous CrF_3, black triangles = Cr_2O_3, yellow stars = Na_2O, violet spades = hydrated KF, magenta crosses = anhydrous KF, full lines = glassy carbon crucibles used, dash lines = alumina crucibles used, dash-dot line = GC inserted into the alumina crucible.

References

[1] V. Pavlík, M. Boča, A. Kityk, Accelerated corrosion testing in molten fluoride salts: Effect of additives and the crucible material, *Corros. Sci.*, 195, 110011 (2022).

[2] V. Pavlík, M. Kontrík, M. Boča, Corrosion behavior of Incoloy 800H/HT in the fluoride molten salt FLiNaK + MF_x (MF_x = CrF_3, FeF_2, FeF_3 and NiF_2), *New J. Chem.*, 39, 9841-9847 (2015).

[3] N.S. Patel, V. Pavlík, B. Kubíková, M. Nosko, V. Danielik, M. Boča, Corrosion behaviour of Ni-based superalloys in molten FLiNaK salts, *Corros. Eng. Sci. Technol.*, 54, 46-53 (2019).

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Low-Energy Electron Interactions with F-Gases Refrigerants

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Montreal protocol [1] have imposed restrictions in the emission of chlorine containing gases to the atmosphere, as the case of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The absence of chlorine or bromine atoms in the molecular structure of hydrofluorocarbons (HFCs) makes such compounds good candidates in replacing CFC and HCFC, leading to an Ozone Depletion Potential value close to zero [2-3]. Tetrafluoroethane, CF_3CH_2F (R134a), a widely used refrigerant gas, has been recognized as a promising substitute for dichlorodifluoromethane, CCl_2F_2 (R12). When R12 is replaced by R134a, the global warming potential drops from 8100 to 1430, the ozone depletion potential changes from 1 to 0, and the atmospheric lifetime decreases from 100 to 14 years [4]. According to the EU Directive 597/2014 [5], R134a was banned in AC systems of vehicles after 2022. One possibility of a substitute gas is the hydrofluoroolefin (HFO), 2,3,3,3-Tetrafluoropropene, $CH_2{=}CFCF_3$, (R1234yf) with 0 ozone depletion potential and a global warming potential of 4, therefore not in the scope of the European legislation related to F-gases.

Fragmentation pathways upon low energy electron interactions to CF_3CH_2F [6-7] and CH_2=CFCF3 were investigated, and the electron ionization (EI) and dissociative electron attachment (DEA) processes have been described, and results are compared. R134a ionization potential was found to be 13.1± 0.2eV whereas R1234yf ionization potential was found to be 11.3 ± 0.1eV. Anion efficiency ion yields will be analysed and compared for both refrigerant gases in the energy range of 0 up to 25 eV. The measurements have been conducted in the crossed electron-molecular beam set-up coupled with ToF-MS. The role of electrons in the dissociation of R134a and R1234yf is described, which is relevant for an improvement of the refrigeration processes as well as in atmospheric chemistry and plasma sciences.

[1] Montreal Protocol on Substances That Deplete the Ozone Layer Montreal C (1989)
[2] A. R. Ravishankara, A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, S. Solomon, *Science*, **1994**, 263, 71-75
[3] S. A. Montzka, R. C. Myers, J. H. Butler, J. W. Elkins, L. T. Lock, A. D. Clarke, A. H. Goldstein, *Geophys. Res. Lett.*, **1996**, 23, 169-172
[4] V. Morcelle, A. Medina, L. C. Ribeiro, I. Prazeres, R. R. T. Marinho, M. S. Arruda, L. A. V. Mendes, M. J. Santos, B. N. C. Tenório, A. B. Rocha, A. C. F. Santos, *J. Phys. Chem. A,* **2018**, 122, 9755-9760, 122, 9755−9760.
[5] Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014
[6] J. Pereira-da-Silva, R. Rodrigues, J. Ramos, C. Brígido, A. Botnari, M. Silvestre, J. Ameixa, M. Mendes, F. Zappa, S. J. Mullock, J. M. M. Araújo, M. T. do N. Varella, L. M. Cornetta, F. Ferreira da Silva*, J. Am. Soc. Mass Spectrom.*, **2021**, 32, 1459-1468
[7] M. Mendes, A. Nunes, J. Pereira-da-Silva, R. Rodrigues, J. M. M. Araújo, F. Ferreira da Silva, L. M. Cornetta *Eur. Phys. J. D., **2022**,* 76, 19

Controlled Synthesis and Properties of Polyvinylidene Fluoride Based Metal-Fluoride Surface Treatments for High-Nickel NCM Cathodes

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Ni-rich cathode materials offer the advantage of reducing cobalt content; however, widely proposed Ni-rich cathode candidates face significant challenges due to their thermal instability and structural deterioration under high-voltage conditions. In particular, when the Ni content exceeds 80 % of the total transition metal in $LiNi_xCo_yMn_{1-x-y}O_2$, the occurrence of the H2-H3 phase transition accelerates material degradation due to irreversible phase transitions during cycling. A common irreversible reaction in Ni-rich cathodes due to the weakening of Ni-O covalent bonds during oxidation of Ni, leading to oxygen reduction reactions and subsequent gas release, which further accelerates material degradation under high voltage. As such degradation predominantly occurs on the particle surface, many previous studies have employed surface coatings with metal cations, which form strong bonds with oxygen in the host structure with suppressing oxygen release. However, coating with high-valence metal ions tends to reduce the initial capacity of the cathode material and hamper the Li+ diffusion kinetics on the interphases. In this study, we present a straightforward coating method using fluorine anions from polyvinylidene fluoride (PVDF) to prevent gas evolution while maintaining the capacity and lithium-ion diffusivity of the nickel-rich $LiNi_{0.96}Co_{0.035}Mn_{0.005}O_2$ cathode.

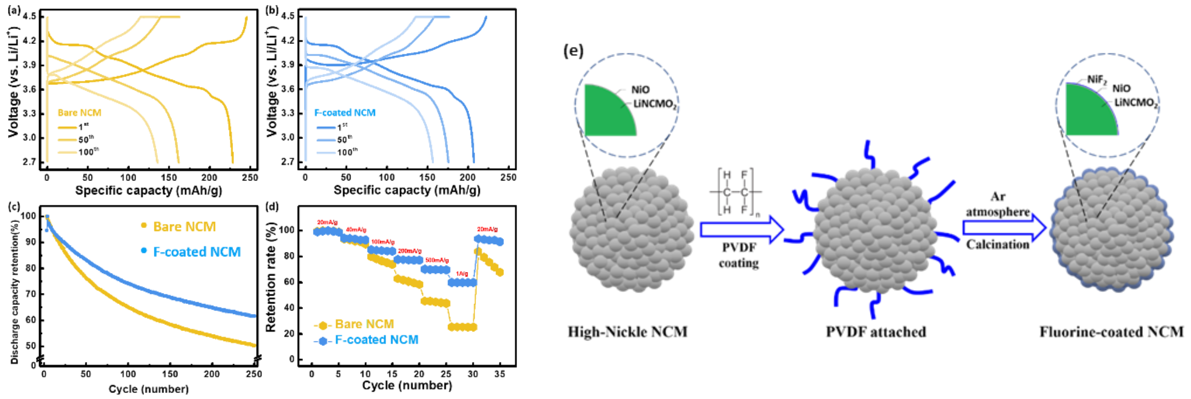

Figure 1. Voltage profiles of bare (a) and fluorine-coated (b) NCMs at denoted cycles. (c) Cycle retention performance of both samples at 200 mA g^{-1} current density. (d) Rate capabilities of both samples. (e) Schematic illustration of the NCM active material Fluorine coating using PVDF.

References

[1] Y.-S. H.; L. P.; X.-Z. L.; Z.-F. M. *J. Fluor. Chem.*, **2007**, *128 (2)*, 139.
[2] A. R. N.; J. Y.; L. *Electrochim. Acta*, **2001**, *46 (15)*, 2293.

New Fluorination Methods of Molybdenum Disulfide (MoS_2) for Enhanced H_2 Production Performances

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Producing green hydrogen without CO_2 emissions is one of the key challenges in the field of sustainable energy. Semiconductor materials, such as transition metal dichalcogenides (TMDs), offer a potential alternative to Pt electrodes for water electrolysis. Among the TMDs, molybdenum disulfide (MoS_2) is gaining increasing interest due to its low cost and high availability combined with interesting physical properties and potential applications (gas detection, energy conversion and storage...).[1] However, its catalytic efficiency is limited by the relatively small number of active sites, as only the edge atoms of MoS_2 are generally considered catalytically active.[2] Doping MoS_2 with fluorine[3] is not widespread, less than 15 articles have been published so far, but it has emerged as a promising approach to enhance the number of active sites and their catalytic activity. Fluorination of MoS_2, typically achieved using ammonium fluoride via solvothermal methods or plasma treatment, induces structural changes (defects, exfoliation, etc.), electronic modifications (conductivity, resistance, etc.) and improved HER performance (only three papers published showing decreases of ≈ 150 mV of the overpotential, and of ≈ 60 for the Tafel slope), even with relatively low fluorine content (generally less than 5 at.%).[4] In this talk, two innovative gas-solid methods of fluorinating MoS_2 will presented: fluorination with $F_2(g)$, occurring via F_2 dissociation, and thermal decomposition of XeF_2, occuring via F• radicals. While F_2 fluorination has only been explored through simulations,[5] fluorination using XeF_2, which was only studied in two papers and offers the potential to produce exfoliated nanosheets with controllable morphology[6].

Here, our aim is to improve the material's catalytic performance by fluorination. A deep understanding of the fluorination mechanisms of F_2 and XeF_2 is going to be presented and was achieved through various characterization techniques, enabling a detailed comparison of the structural and catalytic impacts of each method on MoS_2. Notably, F_2 exhibits significantly higher reactivity with MoS_2 compared to XeF_2. Indeed, fluorination with F_2 results in important etching, high surface area (216 m^2/g vs 10 m^2/g for pristine MoS_2) and oxidation. Both methods, however, induce high fluorination amounts, as high as 30% and 20 % for F_2 and XeF_2 fluorination respectively, which are the highest amounts of F atoms in MoS_2 reported so far. Results also show that fluorinated MoS_2 achieves a hydrogen production rate that is an order of magnitude higher, a reduction in overpotential exceeding 200 mV and a twofold increase in current density compared to pristine MoS_2. All the results highlight an important and specific production of H_2 with the fluorinated MoS_2.

References

[1] Krishnan U., Kaur M., Singh K. et al., *Superlattices Microstruct*. **2019**, 128, 274-297; [2] Abidi N., Bonduelle-Skrzypczak A. and Steinmann S. N. *J.Phy. Chem. C* **2021,** 125 (*31*) 7058–17067; [3] Venkateswarlu G., Madhu D. and Vatsala Rani J., *Func. Mater. Lett*. **2019,** 12(*03*), 1950041 ; [4] Copetti G., Nunes E.H., Feijó T.O. et al., *J. Mater. Chem. C*, **2019**, 7, 14672-14677; [5] Paudyal H., Pantha N. and Prasad Adhikari N., *BIBECHANA,* **2016**, 13, 50–59 ; [6] Huang Y., Wu J., Xu X. et al. *Nano Res*. **2013**, 6 (*3*), 200-207

Fluorinated Soft-Matter – Compartmentalized Micelles, Hemimicelles, Mesophases, Microemulsions and more

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In recent work, we demonstrate how the mutual phobicity between hydrogenated and perfluorinated chains can induce novel types of compartmentalized supramolecular structures. Using a combination of molecular dynamics simulations (MD) and different experimental techniques, we have gained a molecular-level understanding of the structure and dynamics of the obtained structures which allows rationalizing, predicting, and thus controlling, their morphology and properties. Several examples of this approach are presented: the formation of compartmentalized micelles from semifluorinated (SF) surfactants, surfactant mixtures, or surfactant-free microemulsions (SFME); surface hemimicelles of SF alkanes; polar-fluorous-hydrogenous tri-continuous phases in ionic liquids; aneotropy in mixtures of amphipiles; the transition from nano-segregation to phase-separation/mesophases in mixtures of (alkane + perfluoroalkane) or in pure SF alkanes.

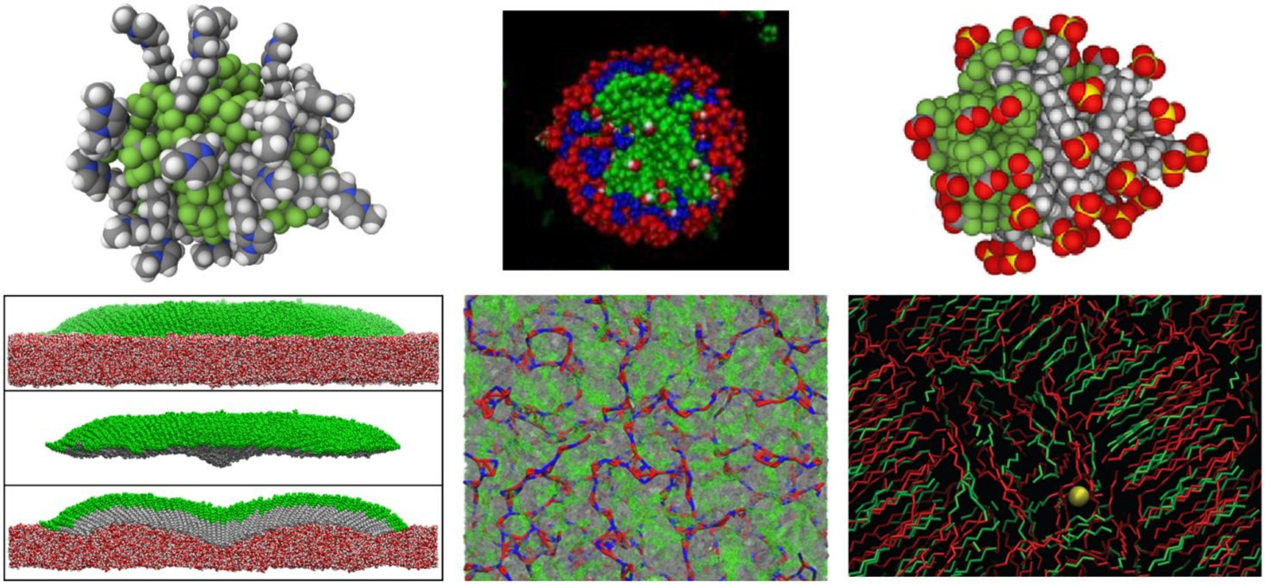

Figure 1. MD Simulation snapshots illustrating: onion-type micelle of a semifluorinated surfactant; onion-type micelle in a water + ethanol + F-alcohol SFME; Janus-type micelle in an aqueous mixture of F- and H-surfactants; three views of an SF alkane hemimicelle; polar-fluorous-hydrogenous tri-continuity in an ionic liquid; mesophase formation in an SF alkane

PARALLEL SESSION III

Contaminants of Emerging Concern (sponsored by ALERT-PFAS)

Functional Material for PFAS Removal

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Per- and polyfluoroalkyl substances (PFAS) have become a critical concern in the field of water remediation due to their pervasive presence and potential health risks. The urgency to develop advanced technologies for capturing and mitigating the impact of PFAS cannot be overstated. Innovative materials specifically designed for the decontamination of water are being created by our team to address this challenge.

The intersection of polymer, supramolecular, colloidal, and inorganic chemistry is leveraged to develop functional, high-performance materials. The unique properties of these disciplines are utilized to design materials with enhanced capabilities. These novel materials are intended to be used in the fabrication of membranes and adsorbents, providing immediate and effective solutions for the selective removal of PFAS from contaminated water sources.

A wide variety of PFAS, regardless of their chain length or functional groups, can be removed by our materials. This includes even the shortest PFAS, such as trifluoroacetic acid (TFA). By targeting a broad spectrum of PFAS compounds, comprehensive water decontamination is aimed to be ensured.

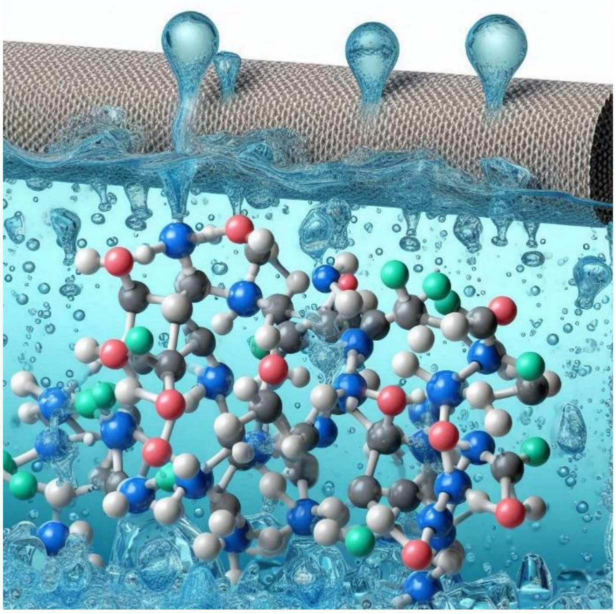

Figure 1. Decontamination of water and PFAS removal using innovative and selective material.

How can PFAS be Photochemically Eliminated from Aquatic Compartments?

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Per- and polyfluoroalkyl substances (PFAS) are persistent organic pollutants widely detected in aquatic environments due to their extensive use and chemical stability [1]. Conventional water treatment technologies, including adsorption and oxidation processes, often fail to achieve complete degradation of PFAS, necessitating the development of more efficient methods [2].
Among emerging approaches, photochemical processes utilizing hydrated electrons (e_{aq}^{-}) have demonstrated promising results for the reductive defluorination of PFAS. Advanced Reduction Processes (ARPs), particularly UV/sulfite and Vacuum Ultraviolet (VUV)/sulfite systems, have been shown to effectively decompose perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The generation of e_{aq}^{-} via sulfite photolysis under UV or VUV irradiation enables the cleavage of the strong C–F bonds, leading to significant mineralization of PFAS into fluoride ions [2, 3].

Recent studies have reported nearly complete PFOS degradation within 4 hours in a VUV/sulfite system, with a defluorination efficiency of around 75%. The process is highly dependent on pH, sulfite concentration, and the presence of co-existing natural organic matter [3]. The effectiveness of VUV/sulfite over UV/sulfite has been attributed to enhanced photolysis and electron transfer mechanisms [3].

Further research is required to optimize process parameters and evaluate the scalability of these methods for large-scale water treatment applications. Understanding the reaction pathways and potential by-product formation remains crucial for the safe and efficient implementation of photochemical PFAS remediation strategies [4]. In this presentation, we will discuss our latest experimental findings, obtained in the coming months, providing new insights into the feasibility and optimization of PFAS photodegradation in aquatic systems.

References

[1] S. Kurwadkar, J. Dane, S. R. Kanel, M. N. Nadagouda, , R. W. Cawdrey, B. Ambade, G. C. Struckhoff, R. Wilkin *Sci. Total Environ.,* **2022**, *809*, 151003.
[2] J. Cui, P. Gao, Y. Deng *Environ. Sci. technol.*, 2020, *54*, 3752-3766.
[3] Y. Gu, T. Liu, H. Wang, H. Han, W. Dong *Sci. Total Environ.,* **2017**, *607-608*, 541-548.
[4] S. Wacławek, X. Ma, V. K. Sharma, R. Xiao, K. E. O'Shea, D. D. Dionysiou *Water Res.*, **2022**, *212*, 118101.

Fluorinated Methane Derivatives Hydrates: a Molecular Simulation study

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Hydrates are non stoychiometric crystalline inclusion solids where a network of water molecules leaves voids in its structure where small guest molecules can be enclathrated. The main interest related with hydrate studies stems for the demonstrated occurrence of huge natural hydrate deposits trapping methane on the ocean seafloor or frozen soils. Also, the formation of hydrates inside pipelines has represented a major challenge in oil industry flow assurance applications. The possibility of using hydrates to selectively capture and store gases has also been a matter of great interest. These applications, among others, have contributed to extensive scientific research intended to characterize the physico-chemical properties of these systems. From a theoretical point of view, the description of the phase equilibria and thermophysical properties of these systems is a challenging task. From a thermodynamic point of view, the solid-gas multiphasic properties of hydrates are poorly described by the commonly used equations of state and macroscopic scale models. In this context, molecular simulation techniques have contributed to a better description and understanding of these systems, providing valuable insight to develop macroscopic models. Molecular Dynamics can provide simultaneous description of atomic scale structure and crystalline geometry, but also description of phase boundaries, and dynamic information as diffusion coefficients and interfacial behaviour.

Methane fluorinated derivatives are known to form hydrates, but their study is by far less developed than those devoted to more popular guest molecules as methane, carbon dioxide or hydrogen to cite a few examples. In this work [1, 2], attention has been paid to the theoretical characterization of hydrates formed by methane fluorinated derivatives. A twofold strategy has been used. First, *ab initio* quantum calculations have been performed to determine the potential energy landscapes within a hydrate cell containing a fluorinated methane as guest molecule. This allows to determine also the energetic barrier the guest molecule faces when diffusing through the hydrate. Then, direct coexistence Molecular Simulation calculations have been performed to evaluate the existing molecular forcefields for these molecules, comparing the results with the scarce existing experimental data. The obteined results evidence that accurate calculations can be performed for these hydrates with only slightly modified molecular models.

References

[1] Fernández-Fernández, Á. M.; Pérez-Rodríguez, M., Piñeiro, M. M. *J. Mol Liq.*, **2020**, *314*, 113783.
[2] Fernández-Fernández, Á. M.; Pérez-Rodríguez, M., Piñeiro, M. M. *J. Mol Liq.*, **2021**, *339*, 116720.

ALERT-PFAS Solutions - Digital Tool for Modelling PFAS Risk in Natural Environments

Albert Serra-Compte,[1*] *Eduard Puga*,[1] *Ioanna Karakatsanidou*,[1] *Sergi Baena*, [1] *Susana González*, [1]

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The occurrence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the environment and specially in inland waters has become a topic of concern. The characteristics of PFASs that make them pollutants of concern are well known, especially their toxicity and persistence in the environment. There are different sources of PFAS to the environment including areas around industrial production, manufacturing and fire-fighting testing sites. Among these, the use of PFAS in fire-fighting foams has emerged as one of the most relevant sources of PFAS only behind the chemical industry. Huge efforts have been made in order to characterize natural sites polluted by PFAS worldwide and facilitate this information through visualization maps. However, the potential PFAS pollution derived from the use of fire-fighting foams is scarcely considered in the already developed visualization maps, nor providing early event detection and recommendations to relevant stakeholders responsible for water bodies management when PFAS pollution risk occurs in their area of influence. In this context, the present study aims at developing a digital tool to inform on PFAS pollution risk in water bodies mainly derived from wildfires to provide early event detection for water management decision-making. The study is being developed under the ALERT-PFAS project that aims at implementing a transnational strategy to detect and prevent the PFAS pollution in the south-west Europe (SUDOE) natural spaces. The tool integrates information from different open sources including, satellite images for land use and wildfires characterization, weather, ground and water quality sensors. The data gathered is modelled to assess the PFAS risk surface water bodies. Then, based on PFAS risk the tool provides early detection events to end-users including water operators, administrations, natural park managers, etc.

Figure 1. Schematic diagram of digital tool data processing

The results provided by the tool will be validated in real case scenarios including different natural parks from the SUDOE area that suffered from wildfires in recent years, allowing for model recalibration and improvement for a better PFAS risk prediction. The solution aims at equipping relevant stakeholders with tools to facilitate addressing the PFAS pollution risk in the most vulnerable areas.

Acknowledgements
ALERT-PFAS - Transnational strategy to detect and prevent PFAS pollution (S1/2.4/P0099). Founded by the European Union - Interreg SUDOE program

Monitoring of PFAS Hotspots and Surface Water Treatment Solutions in Natural Areas

Joana C. Bastos[1], Srdana Kolakovic[1], Beatriz P. Machado[1], Maria G. Vaz[1], Maria C. Naranjo[1], Mona Semsarilar[1], Ana B. Pereiro[1], João M. M. Araújo[1,]*

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Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic chemicals widely used in industrial applications and consumer products for their water- and oil-resistant properties. These substances are commonly found in non-stick cookware, waterproof textiles, food packaging, and industrial processes. The firefighting foams are the second more important source for PFAS contamination, particularly aqueous film-forming foams (AFFFs), which are used to suppress flammable liquid fires. These compounds are highly resistant to degradation, earning them the classification of “forever chemicals”. Once released into the environment, they persist for decades, accumulating in soils, surface waters, and living organisms posing serious risks to both aquatic ecosystems and human health. The ALERT-PFAS project focuses on developing advanced monitoring tools and strategies to detect, assess, and prevent PFAS contamination in natural areas. Wildfires are becoming more frequent and severe due to climate change and can contaminant these natural areas with PFAS, accumulating them in soils, ecosystems, and water bodies. In this work, a mitigation strategy for addressing PFAS contamination in natural areas will be presented, supported by experimental results obtained from field sampling campaigns. Additionally, innovative remediation techniques will be discussed, focusing on the application of high-performance adsorbent materials—specifically activated carbons (ACs), metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). These materials, characterized by their large surface areas and tuneable pore structures, have demonstrated strong potential for the efficient adsorption and removal of PFAS from contaminated water sources. A comprehensive assessment of PFAS detection in natural areas with this advanced remediation technologies allow to obtain efficient a transnational strategy for monitoring and prevention of PFAS contamination. These strategies will contribute to mitigate and prevent the long-term impacts of these persistent pollutants in natural areas and ecosystems.

References

[1] Brunn, H., Arnold, G., Körner, W. et al. PFAS: forever chemicals—persistent, bioaccumulative and mobile. Reviewing the status and the need for their phase out and remediation of contaminated sites. Environ. Sci. Eur. 35, 20 (**2023**). https://doi.org/10.1186/s12302-023-00721-8.

Transnational Strategy for the Detection of PFAS under Alert-PFAS Project

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The Alert-PFAS project aim is to develop and implement a transnational strategy to detect, prevent and mitigate per-and polyfluoroalkyl substances (PFAS) contamination in natural spaces across the SUDOE region. In 2022, wildfires affected natural parks and protected areas [1] and studies show that the highest environmental concentrations of PFAS are commonly associated with firefighting activities due to the extensive use of PFAS in firefighting agents in aqueous film forming foams [2]. In Alert-PFAS project, different institutions work on the development of optical sensors to be implemented in Sudoe area demosites: Spain, France and Portugal. The demosites are rural and natural parks affected by fires in the SUDOE area. Montpellier (France) and UVIGO (Spain) are developing different approaches for the PFAS selective layers for PFAS and IT (Portugal) is developing optical architectures that will accommodate and interrogate the selective layers. In this presentation, the possible optical sensing approaches will be shown, taking advantage of the optical sensors such as compactness, lightweight and immunity to electromagnetic interference [3].

Acknowledgements

The authors would like to acknowledge the funding of the ALERT-PFAS project, S1/2.4/P0099, co-funded by the Interreg Sudoe Program through the European Regional Development Fund (ERDF).
This work was supported by FCT - Fundação para a Ciência e Tecnologia, I.P. by project reference UIDB/50008, and DOI identifier 10.54499/UIDB/50008.

References

[1] Alert-PFAS Interreg Sudoe Website: https://interreg-sudoe.eu/en/proyecto-interreg/alert-pfas/
[2] Reinikainen J., Perkola N., Äystö L., Sorvari J., The occurrence, distribution, and risks of PFAS at AFFF-impacted sites in Finland, *Sci. Total Environ.*, **2022**, *829*,(154237), https://doi.org/10.1016/j.scitotenv.2022.154237.
[3] Pires Duarte D. A., Nogueira R. N., Bilro L., Optical Fiber Sensing Principles. Plastic Optical Fiber Sensors, Science Technology and Applications, CRC Press, **2019**, 67–91, https://doi.org/10.1201/b22357-3

Scientific Programme: Talks

Tuesday, August 5th, 2025

Tuesday, August 5th, 2025

PLENARY SESSION - VERONIQUE GOUVERNEUR

Room: Auditorium II
Chair: Norio Shibata, Nagoya Institute of Technology, Japan

09:00 – 10:00	**RETHINKING FLUORINE CHEMISTRY WITH GLOBAL CHALLENGES IN MIND**
PL	**Veronique Gouverneur**, University of Oxford, UK

KEYNOTE SESSION - BEATE KOKSCH

Room: Auditorium II
Chair: Veronique Gouverneur, University of Oxford, UK

10:00 – 10:45	**FLUOROPEPTIDES AS BIODEGRADABLE BIOPOLYMERS**
KN	**Beate Koksch**, Freie University of Berlin, Germany

PUBLIC DISCUSSION ABOUT PFAS

Room: Auditorium II
Moderator: Rita Santos, Journalist in Biosfera, Farol de Ideias, Portugal

11:15 – 12:15	**ROUNDTABLE 1: POLICY RECOMMENDATIONS FOR CONTAMINANTS OF EMERGING CONCERN**
	Rolf-Jan Hoeve, DG ENVI, European Commission (TBC)
	Veronique Gouverneur, University of Oxford, UK
	Luis Simas, ERSAR, Portugal
	Mark Shiflett, University of Kansas, USA
	Romain Gandre, Veolia, France
	Ronald Bock, AGC, UK
	Vanessa Gouveia, Ambigroup, Portugal

Room: Auditorium II
Moderator: Rita Santos, Journalist in Biosfera, Farol de Ideias, Portugal

12:30 – 13:30	**ROUNDTABLE 2: SUSTAINABLE AND SAFE PFAS FOR HEALTH AND THE ENVIRONMENT**
	Dexi Weng, Dexyan Global, USA Comeall Technology, China/USA
	Nebojša Ilić, PFASuiki GmbH, Germany
	Susana Fonseca, ZERO, Portugal
	Marie-Pierre Krafft, University of Strasbourg, France
	Lourdes F. Vega, Khalifa University, UAE
	Bruno Ameduri, Institute Charles Gerhardt Montpellier, France
	Beate Koksch, Freie University of Berlin, Germany

SESSIONS ON PFAS AND EUROPEAN PROJECT ACTIVITIES

Please check all the information here: **Sessions on PFAS and European Project Activities**

Register here: **https://forms.office.com/e/7p5cYjHEAG**

FUNDING OPPORTUNITIES

Room: 3A
Moderator: Tamara Rodriguez, FEUGA, Spain

14:30 – 16:00	**EUROPEAN FUNDING OPPORTUNITIES** **Bernd Decker** – Head of Sector, CINEA, European Commission **Vanda Pereira from APA (Portuguese Environment Agency)** – Responsible for the LIFE Programme in Portugal **Ana Sutcliffe from ANI (National Innovation Agency)** – Responsible for the Horizon Europe calls in Portugal **Raquel Rocha from AD&C (Agency for Development and Cohesion)** – Responsible for the Interreg calls in Portugal
16:00 – 17:30	**EUROPEAN RESEARCH NETWORKING FORUM**

OPEN FUN HALL

Room: Pavilion 3 Main Hall

14:30 – 18:30	**FUN HALL – INNOVATION, LEARNING AND FUN** **Reading and Discovery Area** **Interactive Games** **Environmental Trivia** **European Project Poster Exhibition** **Cinema Room** **'Aquaville' Game – Protect your City!**

Scientific Programme: Talks

Wednesday, August 6th, 2025

Wednesday, August 6th, 2025

PLENARY SESSION - DEXI WENG

Room: Auditorium II
Chair: Pierangelo Metrangolo, Politechnico di Milano, Italy

09:00 – 10:00	**CALCIUM FLUORIDE (FLUORSPAR) TO PERFLUOROORGANIC MATERIALS TO DATA OPTICALIZATION**
PL	**Dexi Weng**, Dexyan Global, USA Comeall Technology, China/USA

KEYNOTE SESSION - MATTHEW HOPKINSON

Room: Auditorium II
Chair: Petr Beier, Institute of Organic Chemistry and Biochemistry, Czech Republic

10:00 – 10:45	**NOVEL METHODS FOR INSTALLING EMERGING FLUORINATED MOTIFS**
KN	**Matthew N. Hopkinson**, Newcastle University, UK

PARALLEL SESSION IV – ORGANIC CHEMISTRY

Room: Auditorium II
Chair: Mark Crimmin, Imperial College London, UK

11:15 – 11:35	**EXPANDING THE TOOLBOX OF FLUORINATED MOTIFS: SELECTIVE STRATEGIES FOR FLUOROALKYLATION AND PFAS ALTERNATIVES**
IL	**Frédéric R. Leroux**, University of Strasbourg, France
11:35 – 11:55	**A CONVENIENT OXIDATIVE FLUORINATION PROCEDURE TO FORM HYPERVALENT IODINE(V) FLUORIDES**
IL	**Alison M. Stuart**, University of Leicester, UK
11:55 – 12:15	**TRANSITION METAL-CATALYZED DEFLUORINATIVE FUNCTIONALIZATION OF FLUORINATED AND PERFLUOROALKYLATED ALKENES**
IL	**Gavin Chit Tsui**, The Chinese University of Hong Kong, China
12:15 – 12:30	**CAPITALIZING ON OXIME REARRANGEMENT CHEMISTRY FOR THE SYNTHESIS OF UNIQUE FLUORINE-CONTAINING MOTIFS**
Oral	**Patrick R. Melvin**, Bryn Mawr College, USA
12:30 – 12:45	**ORGANIC MOLECULE AGGREGATION AND C-H BOND CLEAVAGE IN POLAR FLUORINATED ARENES**
Oral	**Tianfei Liu**, Nankai University, China
12:45 – 13:00	**EXPLORATION OF NOVEL N-DIFLUOROMETHYL MOTIFS**
Oral	**Gina Wycich**, RWTH Aachen University, Germany
13:00 – 13:15	**SYNTHESIS OF N-TRIFLUOROETHYL AND N-DIFLUOROETHYL AZAPEPTIDES AND AZAPEPTOIDS**
Oral	**Dimitra Kyrko**, Université Paris Saclay, France
13:15 – 13:30	**THE ELECTROSTATIC NATURE OF HYDROGEN BONDING INTERACTIONS BETWEEN RCH_2F AND $RCHF_2$ MOTIFS**
Oral	**Bruno A. Piscelli**, University of Campinas, Brazil

PARALLEL SESSION IV – FLUOROUS TECHNOLOGY & MATERIALS

Room: 3A
Chair: Kazuhiko Matsumoto, Kyoto University, Japan

11:15 – 11:35	**EXPLORING THE FLAMMABILITY LIMITS OF FLUORINATED REFRIGERANT MIXTURES USING ARTIFICIAL NEURAL NETWORKS AND MOLECULAR DESCRIPTORS**
IL	**Fèlix Llovell**, Universitat Rovira i Virgili, Spain
11:35 – 11:55	**AG(II)-BASED MAGNETIC PRECURSORS OF NOVEL SUPERCONDUCTORS**
IL	**Wojciech Grochala**, University Warsaw, Poland
11:55 – 12:15	**INTERFACIAL MOLECULAR ENGINEERING FOR FUNCTIONAL MATERIALS: NEW DESIGN PRINCIPLE FOR MATERIALS WITH PERMEABLE PROPERTIES**
IL	**Yoshimitsu Itoh**, The University of Tokyo, Japan
12:15 – 12:35	**EXPLORING SUPRAMOLECULAR CHEMISTRY AND PHOTOREDOX CATALYSIS WITH PFASS AND IN PFASS**
IL	**Jean-Marc Vincent**, University of Bordeaux, France
12:35 – 12:50	**PERFLUOROPOLYETHER-FUNCTIONALIZED CARBON-BASED MATERIALS AND THEIR APPLICATIONS IN ENERGY DEVICES**
Oral	**Maurizio Sansotera**, Politecnico di Milano, Italy
12:50 – 13:05	**LEVERAGING MOLECULAR THERMODYNAMICS AND MACHINE LEARNING FOR THE RATIONAL DESIGN OF ALTERNATIVE REFRIGERANT BLENDS**
Oral	**Ismail I. I. Alkhatib**, Khalifa University, United Arab Emirates
13:05 – 13:20	**COMPUTATIONAL MODELLING OF THE GLOBAL WARMING POTENTIAL CLIMATE METRIC ACROSS FLUORINATED MOLECULES**
Oral	**Luís P. Viegas**, Universidade de Coimbra, Portugal
13:20 – 13:35	**CHIRAL FLUOROALKYLIMINES IN ASYMMETRIC SYNTHESIS: ADVANCES AND APPLICATIONS**
Oral	**Yuliya Rassukana**, National Academy of Sciences of Ukraine, Ukraine

PARALLEL SESSION IV – CONTAMINANTS OF EMERGING CONCERN

Room: 3B
Chair: Valentina Dichiarante, Politecnico di Milano, Italy

11:15 – 11:35	**WHAT DO WE KNOW ABOUT PER- OR POLYFLUOROALKYL SUBSTANCES (PFASS)? ISSUES, CHALLENGES, REGULATIONS AND POSSIBLE ALTERNATIVES**
IL	**Bruno Ameduri**, Institut Charles Gerhardt, France
11:35 – 11:55	**FIREFIGHTERS' OCCUPATIONAL EXPOSURE TO PER- AND POLYFLUOROALKYL SUBSTANCES**
IL	**Marta Oliveira**, Instituto Superior de Engenharia do Porto, Portugal
11:55 – 12:15	**BREAKING THE CHAINS OF PFAS WITH ELECTROCHEMICAL OXIDATION – THE SUIKI BOTTOM-UP APPROACH**
IL	**Nebojša Ilić**, PFASuiki GmbH, Germany
12:15 – 12:30	**PFAS DEGRADATION DURING HAZARDOUS WASTE INCINERATION: A PILOT-SCALE STUDY WITH COMPREHENSIVE ANALYTICAL APPROACH**
Oral	**Muckensturm Gaël**, Veolia Research and Innovation, France

12:30 – 12:45	**PFAS REMOVAL FROM LANDFILL LEACHATES WITH AN ELECTROCHEMICALLY ASSISTED NANOFILTRATION MEMBRANE**
Oral	**Ane Urtiaga**, University of Cantabria, Spain
12:45 – 13:00	**COMPARISON OF PFAS CONTAMINATION BETWEEN TWO EUROPEAN AND ASIAN RIVERS**
Oral	**Khanh Vu**, Aix-Marseille University, France
13:00 – 13:15	**PFAS AND WATER RESOURCES: HOW TO DETERMINE THE BEST TREATMENT SOLUTION?**
Oral	**Romain Gandré**, Veolia, France
13:15 – 13:30	**REMOVAL OF PFAS FROM WATER BY ADSORPTION: RECENT PROGRESS AND FUTURE PERSPECTIVES**
Oral	**Daniel Dianchen Gang**, University of Louisiana at Lafayette, USA

PARALLEL SESSION V – ORGANIC & ORGANOMETALLIC CHEMISTRY

Room: Auditorium II
Chair: Jason Dutton, La Trobe University, Australia

14:30 – 14:50	**SELECTIVE FLUORINATED DEELECTRONATORS AND ORGANOMETALLIC METAL-DIMERS: A REACTIVE COUPLE TO ACCESS UNKNOWN CATIONS…**
IL	**Ingo Krossing**, University of Freiburg, Germany
14:50 – 15:10	**DEHYDROFLUORINATION OF LEGACY REFRIGERANTS AT GROUP 9 METAL PINCER COMPLEXES**
IL	**David A. Vicic**, Lehigh University, USA
15:10 – 15:30	**SYNTHETIC REACTIONS OF ISOLATED TRIFLUOROMETHYL ISOBENZOFURANS**
IL	**Hideki Amii**, Gunma University, Japan
15:30 – 15:45	**REVERSED ELECTROSTATIC DESIGN FOR SELECTIVE RECOGNITION OF BTX VIA Π-HOLE···Π INTERACTIONS BY A TETRAOXA[2]PERFLUOROARENE[2]TRIAZINE HOST**
Oral	**Akiko Hori**, Shibaura Institute of Technology, Japan
15:45 – 16:00	**[(TRIISOPROPYLSILYL)ACETYLENE]SULFUR PENTAFLUORIDE – A VALUABLE REAGENT FOR ACCESSING UNPRECEDENTED CLASSES OF SF_5-CONTAINING BUILDING BLOCKS**
Oral	**David Rombach**, University of Zurich, Switzerland
16:00 – 16:15	**UNUSUAL ROLE OF HEXAFLUOROISOPROPANOL IN REDOX-ACTIVATED CYCLOADDITIONS**
Oral	**Michał J. Jadwiszczak**, University of Warsaw, Poland
16:15 – 16:30	**NEW ACCESS ROUTES TOWARD THIOCARBAMOYL FLUORIDES AND TRIFLUOROMETHANESULFENAMIDES USING AN EASY-TO-USE AND SHELF-STABLE CF_3S-REAGENT**
Oral	**Clément Delobel**, Institute of chemistry and biochemistry (ICBMS), France
16:30 – 16:45	**A NEW SULFOXIMINE SCAFFOLD FOR THE GENERATION OF DIVERSE FLUORINATED RADICALS IN PHOTOREDOX CATALYSIS**
Oral	**Gabriel Goujon**, Institut Lavoisier de Versailles - UVSQ, France
16:45 – 17:00	**STEREOSELECTIVE SYNTHESIS OF (2S,4S)-5,5,5,5′,5′-PENTAFLUOROLEUCINE AND (2S,4R)-5,5,5-TRIFLUOROLEUCINE**
Oral	**Sandeep Mummadi**, European Institute of Chemistry and Biology (IECB), France

17:00 – 17:15 Oral	**ENANTIOSELECTIVE CONSTRUCTION OF A FLUORINATED TERTIARY CARBON USING PRIMARY AMINE CATALYSTS** **Satoru Arimitsu**, University of the Ryukyus, Japan

PARALLEL SESSION V – ORGANIC CHEMISTRY

Room: 3A
Chair: Thierry Billard, CNRS - University of Lyon, France

14:30 – 14:50 IL	**UPGRADING THE HALOGEN BOND DONOR ABILITY OF ORGANIC FLUOROARENES** **Giuseppe Resnati**, Politecnico di Milano, Italy
14:50 – 15:10 IL	**CATALYST FREE O-ARYLATION REACTIONS OF FLUOROBENZENES** **Frederik Diness**, Roskilde University, Denmark
15:10 – 15:25 Oral	**ACTIVATION OF AROMATIC CARBON¬–FLUORINE BONDS: COUPLING REACTION OF FLUOROBENZOFURANS** **Junji Ichikawa**, Sagami Chemical Research Institute, Japan
15:25 – 15:40 Oral	**POLYFLUOROALKOXYLATION OF DIARYLIODONIUM SALTS VIA ELIMINATIVE LIGAND COUPLING USING POLYFLUOROALKOXY BORATE SALTS** **Kotaro Kikushima**, Ritsumeikan University, Japan
15:40 – 15:55 Oral	**SELECTIVE C(SP^3)–F BOND FUNCTIONALIZATION OF TRIFLUOROMETHYL ARENES UTILIZING EDA COMPLEX** **Takahiko Akiyama**, Gakushuin University, Japan
15:55 – 16:10 Oral	**FUNCTIONAL GROUP TRANSFORMATION AT C5 POSITION OF FLUORINATED ISOXAZOLINES VIA C-F BOND CLEAVAGE** **Kazuyuki Sato**, Setsunan University, Japan
16:10 – 16:25 Oral	**PHOTOACID-INDUCED ADDITION OF KETENE SILYL ACETALS TO FLUORINATED LSOCOUMARINS AND DEFLUORINATIVE RING REARRANGEMENT OF THE ADDUCTS** **Hikaru Yanai**, Tokyo University of Pharmacy and Life Sciences, Japan

PARALLEL SESSION V – INORGANIC CHEMISTRY, COMPUTATIONAL CHEMISTRY & BIOORGANIC & MEDICINAL CHEMISTRY

Room: 3B

Chair: Rodrigo Cormanich, Universidade Estadual de Campinas, Brazil

14:30 – 14:50	**BIS(TRIFLUOROMETHYL)AMINES – SYNTHESIS & PROPERTIES**
IL	**Maik Finze**, University of Wurzburg, Germany
14:50 – 15:10	**WHY FINDING THE PERFECT SUSTAINABLE REFRIGERANT IS HARDER THAN YOU THINK**
IL	**Lourdes F. Vega**, Khalifa University of Science and Technology, United Arab Emirates
15:10 – 15:25	**THE FLUORINASE – PAST, PRESENT AND FUTURE**
Oral	**Phillip T. Lowe**, University of St Andrews, UK
15:25 – 15:40	**NEW AVENUES IN ORGANOXENON CHEMISTRY**
Oral	**Alberto Pérez-Bitrián**, Humboldt-Universität zu Berlin, Germany
15:40 – 15:55	**PENTAFLUOROPHOSPHATES AS BIOMIMETICS OF PHOSPHOPEPTIDES AND PHOSPHOPROTEINS**
Oral	**Anna Magdalena Ambros**, Freie Universität Berlin, Germany
15:55 – 16:10	**SYNTHESIS AND REACTIVITY OF FLUORINATED ALKYL HALONIUM IONS**
Oral	**Lukas Fischer**, Freie Universität Berlin, Germany
16:10 – 16:25	**PHOSPHONATE ANALOGUES OF FLUOROPHENYLGLYCINES AS POTENTIAL INHIBITORS OF HUMAN UROKINASE PLASMINOGEN ACTIVATOR: SYNTHESIS, STRUCTURE AND ANTICANCER ACTIVITY**
Oral	**Donata Pluskota-Karwatka**, Adam Mickiewicz University in Poznań, Poland
16:25 – 16:40	**FLUORINATION OF ROTAXANES FOR SENSITIVE 19F MR-FLUORESCENCE DUAL IMAGING**
Oral	**Zhong Xing Jiang**, Chinese Academy of Sciences, China
16:40 – 16:55	**PHOSPHONIUM SF_5- SALTS DERIVED FROM SF_6 AS OXIDATIVE FLUORINATION AND DEOXYFLUORINATION AGENTS**
Oral	**Kim Schramke**, Department of General, Inorganic and Theoretical Chemistry, Austria

PARALLEL SESSION IV

Organic Chemistry

Expanding the Toolbox of Fluorinated Motifs: Selective Strategies for Fluoroalkylation and PFAS Alternatives

*Frédéric R. Leroux**

Université de Strasbourg, CNRS, UMR7042-LIMA, ECPM, 25 rue Becquerel, Strasbourg 67087, France

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Fluorinated groups are omnipresent in bioactive compounds due to their profound influence on key physicochemical properties. Strategically incorporating fluorinated chains allows fine-tuning of lipophilicity, while metabolic stability and biological activity can be markedly enhanced through targeted fluorination.[1]

Our research has long focused on the synthesis of functionalized heteroarenes bearing emerging fluorinated substituents. One of our key approaches leverages fluoroalkylated amine reagents (FARs) as powerful and versatile tools for the regioselective introduction of fluorinated motifs.[2]

Building on this, we recently developed SO_2F_2-mediated fluoroalkylation strategies based on the activation of fluorinated alcohols. [3] This approach enables selective *N*- and *O*-polyfluoroalkylation, unlocking valuable fluorinated building blocks with high relevance in life sciences. In parallel, we have pioneered direct deprotonative functionalization of the difluoromethyl group, providing streamlined access to difluoromethylene-containing compounds with enhanced chemical properties.[4]

Beyond these synthetic advancements, we are also actively exploring sustainable alternatives to fluorinated substituents that fall under PFAS regulations. Here, we will present our latest results in this emerging field, highlighting promising strategies for next-generation fluorine chemistry.[5]

References

[1] S. Pazenok, D. Bernier, M. Donnard, G. Hanquet, A. Panossian, F. R. Leroux, *Modern Fluorine-Containing Agrochemicals*, in *PATAI'S Chemistry of Functional Groups*, **2022**, pp. 1-77.

[2] E. Schmitt, A. Panossian, J. P. Vors, C. Funke, N. Lui, S. Pazenok, F. R. Leroux, *Chem. Eur. J.* **2016**, *22*, 11239-11244; b) E. Schmitt, B. Commare, A. Panossian, J. P. Vors, S. Pazenok, F. R. Leroux, *Chem. Eur. J.* **2018**, *24*, 1311-1316.

[3] L. Santos, M. Donnard, A. Panossian, J. P. Vors, P. Jeschke, D. Bernier, S. Pazenok, F. R. Leroux, *J. Org. Chem.* **2022**, *87*, 2012-2021; b) L. Santos, F. Audet, M. Donnard, A. Panossian, J. P. Vors, D. Bernier, S. Pazenok, F. R. Leroux, *Chem. Eur. J.* **2023**, *29*, e202300792; c) C. Plaçais, L. Wisson, I. Chataigner, M. Donnard, A. Panossian, J.-P. Vors, D. Bernier, S. Pazenok, F. R. Leroux, *Org. Lett.* **2024**.

[4] L. Santos, A. Panossian, M. Donnard, J. P. Vors, S. Pazenok, D. Bernier, F. R. Leroux, *Org. Lett.* **2020**, *22*, 8741-8745; b) A. Messara, N. Vanthuyne, P. Diter, M. Elhabiri, A. Panossian, G. Hanquet, E. Magnier, F. R. Leroux, *Eur. J. Org. Chem.* **2021**, *2021*, 5019-5026; c) A. Messara, A. Panossian, K. Mikami, G. Hanquet, F. R. Leroux, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215899.

[5] F. Audet, M. Donnard, A. Panossian, P. M. Holstein, D. Bernier, S. Pazenok, F. R. Leroux, *Adv. Synth. Catal.* **2024**, *366*, 3466-3473.

A Convenient Oxidative Fluorination Procedure to Form Hypervalent Iodine(V) Fluorides

*Samuel M. G. Dearman,[1] Xiang Li,[2] Yang Li,[2] Kuldip Singh[1] and Alison M. Stuart[1],**

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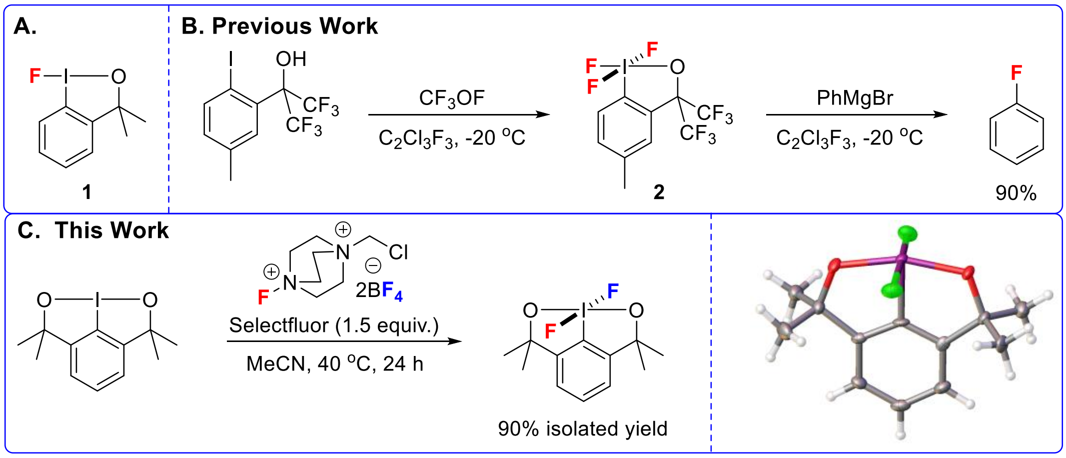
Hypervalent iodine(III) fluorides, like fluoroiodane **1**,[1] are useful fluorinating reagents which display different selectivity to classic electrophilic fluorinating reagents such as Selectfluor and over the last decade they have played an important role in developing new synthetic methodology for creating C-F bonds.[2-3] In 1979 Amey and Martin fluorinated phenylmagnesium bromide with hypervalent iodine(V) fluoride **2** to form fluorobenzene in 90% yield (Scheme 1B).[4] Surprisingly, this potentially useful fluorinating reagent has not been investigated further and the ability to investigate hypervalent iodine(V) fluorides has been limited primarily by their difficult preparation traditionally using harsh fluorinating reagents such as trifluoromethyl hypofluorite and bromine trifluoride. Here, we report a mild and efficient route to deliver hypervalent iodine(V) fluorides in good isolated yields using Selectfluor (Scheme 1C).[5]



Scheme 1. A. Fluoroiodane **1**; **B.** Synthesis and reaction of hypervalent iodine(V) fluoride **2**. **C.** Oxidative fluorination using Selectfluor.

References

[1] Geary, G.C.; Hope, E. G.; Singh, K.; Stuart, A. M. *Chem. Commun*., **2013**, *49*, 9263–9265.
[2] Geary, G. C.; Hope, E. G.; Stuart, A. M. *Angew. Chem. Int. Ed. Engl.*, **2015**, *54*, 14911-14914.
[3] Riley, W.; Jones, A.; Singh, K.; Browne, D. L.; Stuart, A. M. *Chem. Commun*., **2021**, *57*, 7406-7409.
[4] Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc*., **1979**, *101*, 5294–5299.
[5] Dearman, S. M. G.; Li, X.; Li, Y.; Singh, K.; Stuart, A. M. *Beilstein J. Org. Chem*., **2024**, *20*, 1785-1793.

Transition Metal-Catalyzed Defluorinative Functionalization of Fluorinated and Perfluoroalkylated Alkenes

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Methods for introducing fluorine or fluorine-containing groups into organic molecules have been relatively mature which are widely used for the synthesis of valuable organofluorine compounds. Alternatively, the selective cleavage and functionalization of C-F bonds in poly- or perfluorinated molecules constitute an attractive approach to access fluorinated compounds with unique advantages. In this presentation, we will disseminate the recent efforts in our research group for developing the defluorinative functionalization strategy via transition metal catalysis. By utilizing *gem*-difluoroalkenes and perfluoroalkyl alkenes as versatile building blocks, a diverse array of transformations can be achieved to convert a C-F bond into C-C or C-heteroatom bonds with excellent selectivities.

References

ACS Catal. **2021**, *11*, 4799; *Angew. Chem. Int. Ed.* **2020**, *59*, 11293; *Org. Lett.* **2021**, *23*, 5241; *Org. Lett.* **2021**, *23*, 8072; *Org. Lett.* **2020**, *22*, 5193; *Org. Lett.* **2023**, *25*, 2333; *Org. Lett.* **2023**, *25*, 4406; *Org. Chem. Front.* **2024**, *11*, 4366.

Acknowledgement

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Capitalizing on Oxime Rearrangement Chemistry for the Synthesis of Unique Fluorine-Containing Motifs

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Fluorine has quickly grown to be a near essential element in drug design, often appearing in multiple places in some of the most prominent and successful pharmaceuticals. To facilitate this development, chemists have been tasked with devising fluorination protocols that can place this powerful element in various positions on organic molecules. Our research group has recently designed a novel sulfur(VI) – fluorine reagent, known as sulfone iminium fluoride (SIF), that has shown a strong propensity for deoxyfluorination methodologies.[1] The potent reactivity of the SIF reagent facilitates the rapid synthesis of a variety of fluorinated motifs, including alkyl, acyl and phosphinic fluorides.[1,2]

To further show the usefulness of the SIF reagent, our group recently enacted multiple investigations into oxime rearrangement chemistry facilitated by this powerful sulfur(VI) – fluorine molecule. First, we demonstrated that ketoxime substrates could be taken to imidoyl fluorides via a modified Beckmann rearrangement.[3] Notably, these reactions require only 60 seconds to reach quantitative yields of the fluorinated product at room temperature. Next, we endeavoured to apply this chemistry to a less studied oxime substrate: amidoximes.[4] By combining an acid chloride oxime with an amine, we could generate amidoxime substrates *in situ*, which could then be converted to fluoroformamidines when subjected to SIF. Fluoroformamidines are a critically understudied and underutilized functional group, largely due to a dearth of effective and practical synthetic methods. In this work, we provide facile and tuneable access to over 30 unique iterations of this fluorine-containing moiety. Overall, we have continued to show the utility of our SIF reagent by mediating oxime rearrangements for the synthesis of imidoyl fluorides and fluoroformamidines.

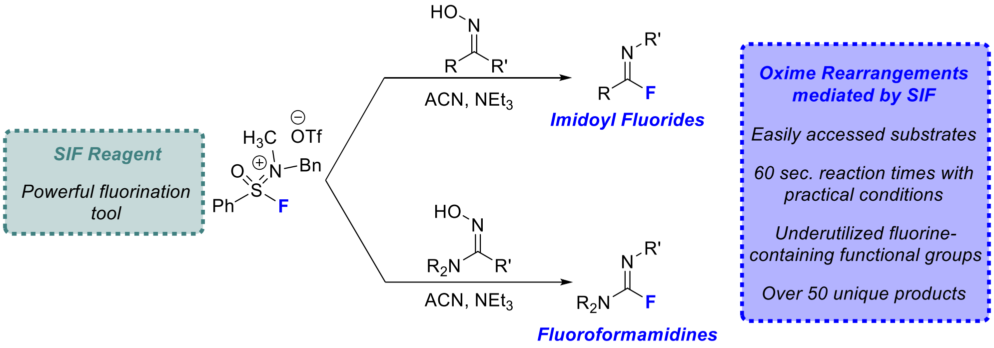

Figure 1. Oxime rearrangements mediated by sulfone iminium fluoride reagent.

References

[1] Vogel, J. A.; Hammami, R.; Ko, A.; Datta, H.; Eiben, Y. N.; Labenne, K. J.; McCarver, E. C.; Yilmaz, E. Z.; Melvin, P. R. *Org. Lett.* **2022**, *24*, 5962.
[2] Miller, L. P.; Vogel, J. A.; Harel, S.; Krussman, J. M.; Melvin, P. R. *Org. Lett.* **2023**, *25*, 1834.
[3] Vogel, J. A.; Krussman, J. M.; Miller, K. F.; Shin, E.; Melvin, P. R. *RSC Adv.* **2023,** *13*, 30129.
[4] Vogel, J. A.; Miller, K. F.; Shin, E.; Krussman, J. M.; Melvin, P. R. *Org. Lett.* **2024**, *26*, 1277.

Organic Molecule Aggregation and C-H Bond Cleavage in Polar Fluorinated Arenes

Tianfei Liu [1,2]*

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An organic molecule's C-H bond cleavage is an important step in the direct functionalization reactions. Recent studies have shown that polar fluorinated arenes such as trifluorotoluene and fluorobenzene promote such reactions. [1,2,3] It has recently been discovered that organic radical molecules can aggregate in these fluorocarbon-hydrocarbon amphiphilic solvents, and that the substituted functional groups can regulate such aggregation behaviours.[4] The aggregation shuttle effect, which accelerates organic chemical reactions in these aggregates, was also discovered. To determine the free energy change associated with the cleavage of the C-H bond in organic compounds in such solvents, a new anchor compound that avoided aggregation was designed and synthesized, which allowed experiments and theoretical calculations to accurately determine the pKa of C-H acids in these solvents.[5] The aggregation behaviours of other organic compounds in such solvents and their influences on organic reactions are still being studied.

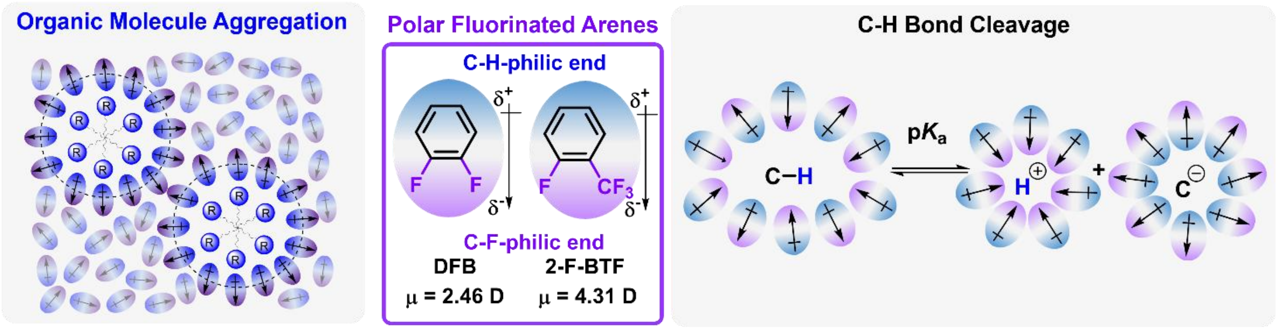

Figure 1. Organic molecule aggregation and C-H bond cleavage in polar fluorinated arenes

References

[1] Fazekas, T. J.; Alty, J. W.; Neidhart, E. K.; Miller, A. S.; Leibfarth, F. A.; Alexanian, E. J. *Scicence,* **2022**, *375*, 545-550.
[2] Lu, Z.; Ju, M.; Wang, Y.; Meinhardt, J. M.; Martinez Alvarado, J. I.; Villemure, E.; Terrett, J. A.; Lin, S. *Nature*, **2023**, *619*, 514-520.
[3] Lu, Z.; Putziger, J.; Lin, S. *Nat. Chem.,* **2025**. https://www.nature.com/articles/s41557-025-01749-4.
[4] Liu, S.; Yang, Y.; Liu, T. *Aggregate*, **2024**, *5*, e543.
[5] Kong, X.; Liang, Y.; Guo, Z.; Lin, T.; Liu, S.; Liu, Z.; Liu, T.; Cheng, J.-P. *ChemSusChem,* **2024**, e202402041.

EXPLORATION OF NOVEL *N*-DIFLUOROMETHYL MOTIFS

Gina Wycich,[1] *Filip G. Zivkovic*,[1] *Jaime Ponce-de-León*,[1] *Linhao Liu*,[1] *Franziska Schoenebeck*[1,*]

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The introduction of fluorine atoms has become a frequently used tool to alter a molecule's properties. Particularly, in medicinal chemistry approximately 20% of all marketed pharmaceuticals contain at least one fluorine atom.[1] Throughout the last decades, the trifluoromethyl group has especially gained a lot of attention and has proven to have a substantial impact on properties like solubility, conformation, lipophilicity, and metabolic stability.[2] Recently, the difluoromethyl group has emerged as a powerful alternative, serving as a suitable bioisostere for alcohol, thiol and amine groups, since its strongly polarized C-H bond allows for efficient hydrogen-bonding.[3] As a result of the scarcity of synthetic methodologies to implement this motif, it has not been explored to the full extent yet. Since nitrogen is extraordinarily abundant in biologically relevant compounds, synthetic means to modify the features of amides and their relatives are therefore highly sought after.[4] We envisioned that by linking these moieties, one could access previously untapped synthetic space, hence realizing undisclosed chemical properties. This presentation showcases our recently developed method which allows for facile access towards *N*-difluoromethyl carbamoyl fluorides. The motif can be further employed as a powerful building block enabling straightforward derivatization towards *N*-difluoromethyl amides, (thio)carbamates, ureas and formamides.[5] Furthermore, we have investigated their properties including lipophilicities and rotational barriers and show their robustness in post-modifications.

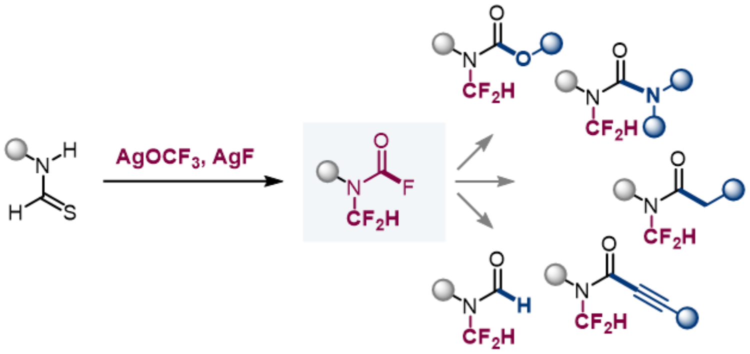

Figure 1. Access towards the *N*-difluoromethyl carbonyl family.

References

[1] Inoue, M.; Sumii, Y.; Shibata, N.; *ACS Omega* **2020**, *5 (19)*, 10633–10640.
[2] Scattolin, T.; Bouayad-Gervais, S.; Schoenebeck, F.; *Nature* **2019**, *573*, 102–107.
[3] Sap, J. B. I.; Meyer, C. F.; Straathof, N. J. W.; Iwumene, N; am Ende, C. W.; Trabanco, A. A.; Gouverneur, V.; *Chem. Soc. Rev.*, **2021**, *50*, 8214-8247.
[4] Pattabiraman, V. R.; Bode, J. W.; *Nature* **2011**, *480*, 471–479.[5] Zivkovic, F. G.; Wycich, G.; Liu, L.; Schoenebeck, F.; *J. Am. Chem. Soc.* **2024**, *146*, 1276–1281.

Synthesis of *N*-Trifluoroethyl and *N*-Difluoroethyl Azapeptides and Azapeptoids

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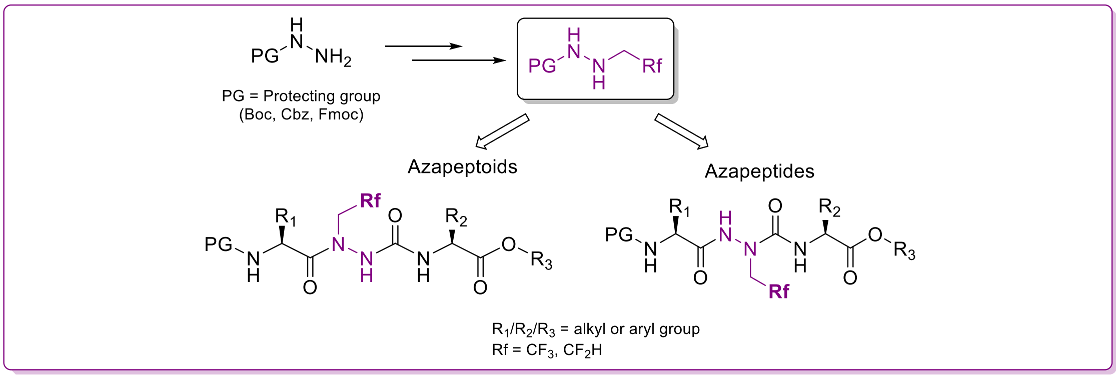
Fluorine has become increasingly prominent in medicinal chemistry due to its particular physicochemical properties, which enhance the therapeutic potential of drug candidates and serve as effective ^{19}F NMR probes. A promising approach to harness fluorine's potential is its incorporation into peptide-based drugs, such as azapeptides and azapeptoids. This class of peptidomimetics, characterized by aza-amino acids in which the α-carbon is replaced by nitrogen, are particularly valuable for optimizing structural and conformational properties in biomedical[1] and biomaterial applications.[2] Notably, the synthesis of $RfCH_2N$-substituted azapeptides and azapeptoids remains unexplored.

Our research focuses on the synthesis of novel peptidomimetics incorporating CF_3CH_2NH- and CF_2HCH_2NH-groups. The initial phase of this study involved the synthesis of fluorinated, functionalized dipeptides through the coupling of fluorinated hydrazines with natural amino acids. The notably low nucleophilicity of the nitrogen bearing the $RfCH_2$- chain required optimization of the coupling conditions. The resulting motifs were further extended in solution using different synthetic approaches to obtain the desired fluorinated peptidomimetics with alkyl and aryl side chains (Scheme 1). NMR and X-ray crystallography analyses were performed to evaluate the influence of fluorinated groups on peptidomimetic conformation.



Scheme 1. CF_3CH_2NH- and CF_2HCH_2NH-substituted azapeptides and azapeptoids

References:
[1] C.; Proulx, J.; Zhang, D.; Sabatino, S.; Chemtob, H. Ong, W. D.; Lubell, *Biomedicines*, **2020**, *8*, 241.
[2] S. D.; Melton, E. A. E.; Brackhahn, S. J.; Orlin, P.; Jin, D. M.; Chenoweth, *Chem. Sci.*, **2020**, *11*, 10638–10646.

The Electrostatic Nature of Hydrogen Bonding Interactions Between RCH_2F and $RCHF_2$ Motifs

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We report computational insights into the hydrogen bond donor ability of CH_2F and CHF_2 motifs, using Cl^- as an acceptor probe and ethane as a model system. Progressive fluorination of ethane has an unexpected impact on atomic charges: geminal hydrogens (H_α) become less positive, while vicinal hydrogens (H_β) gain charge, and fluorinated carbons (C_α) become more electropositive, whereas β-carbons (C_β) become more negative. In fluoroethane, interactions through H_β (-8.67 kcal mol^{-1}) counterintuitively dominate over H_α (-7.12 kcal mol^{-1}). In difluoroethane, the highly charged C_α strengthens bonding through CHF_2 (-10.54 kcal mol^{-1}) over H_β (-9.69 kcal mol^{-1}). The concept of β-H and α-C polarization by fluorination was used to extend the study to all-*cis* C_6 rings. We found the previously synthesized C_6-CF_3 to be a particularly strong Cl^- binder (-47.5 kcal mol^{-1}),[1] outperforming all-*cis* hexafluorocyclohexane (-37.9 kcal mol^{-1}).[2] A newly proposed C_6-CHF_2, where CHF_2 acts as a directional "claw" for anion binding, also exhibits high Cl^- affinity (-39.8 kcal mol^{-1}).

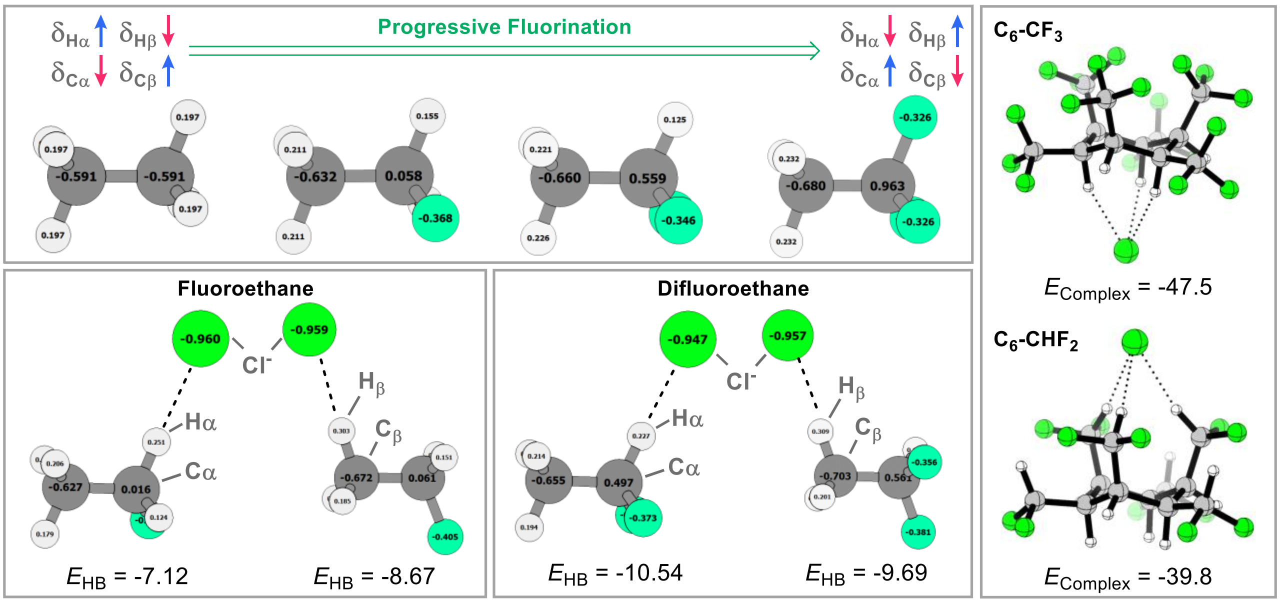

Figure 1. NPA atomic charges in au. Energies in kcal mol^{-1}.

References

[1] Bühl, M.; O'Hagan, D.; *et al. Angew. Chem. Int. Ed.*, **2020**, *59(45)*, 19905-19909.
[2] O'Hagan, D.; McMahon, T. B.; *et al. J. Am. Chem. Soc.*, **2016**, *138(24)*, 7460-7463.

PARALLEL SESSION IV

Fluorous Technology and Materials

Exploring the Flammability Limits of Fluorinated Refrigerant Mixtures Using Artificial Neural Networks and Molecular Descriptors

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With the growing concerns surrounding climate change, the regulation and management of refrigerants with high Global Warming Potential (GWP) refrigerants have become a focal point of attention in recent years. In this regard, the European Union, has led the charge in this direction, aiming to reduce hydrofluorocarbon (HFC) emissions by two-thirds by 2030As the EU's mandates to phase out high-GWP refrigerants come into effect. Consequently, the refrigeration industry is facing a new challenge: the introduction of more flammable yet environmentally compliant alternatives. This paradigm shift amplifies the need for a rapid, reliable screening methodology to assess the propensity for flammability of emerging 4th generation blends, offering a pragmatic alternative to the laborious and time-intensive traditional experimental assessments.

In this study, an Artificial Neural Network (ANN) is constructed, evaluated, and validated to address this challenge, by predicting the Normalized Flammability Index (NFI) for an extensive array of pure, binary, and ternary mixtures, reflecting a substantial diversity of compounds like HFCs, HFOs, sHCs, HOs, and CO_2. An extensive database including 20 pure-components, 1500 binary, and 1607 ternary blends has been compiled, with a wide spectrum of flammability characteristics, and used for ANN model training, testing, and validation. The developed ANN model employed 61 molecular descriptors based on the σ-profile obtained from COSMO-RS, with the optimal configuration of two hidden layers. The optimal configuration has demonstrated a profound fit to the data, with metrics like R^2 of 0.999, RMSE of 0.1735, AARD% of 0.8091, and SDav of ± 0.0434. Exhaustive assessments are conducted to ensure the most efficient architecture without compromising accuracy. Additionally, the analysis of Standardized Residuals (SDR) and Applicability Domain (AD) exhibit fine control and consistency over the data points.

External validation using quaternary mixtures further attests to the model's adaptability and predictive capability. In particular, the impact of mixtures of the combination of fluorinated and non-fluorinated substances is evaluated and interpreted. The model successfully predicts the behavior of prospective industry-relevant mixtures, opening doors to experimentation with untested blends [1].

Acknowledgments. *This work was done in the framework of projects NEW-F-Tech (Ref: TED2021-130959B-I00) and REFCICLA (Ref: PID2023-149713OB-I00) funded by MICIU/AEI/10.13039/501100011033/ and by the European Union NextGenerationEU/ PRTR, as well as projects RC2-2019-007 and RIG-2024-041, funded by Khalifa University of Science and Technology. Additional funding from AGAUR as a Consolidated Research Group (SGR 2021-00738) is appreciated*.

References

[1] C. G. Albà, I.l I Alkhatib, L.F. Vega, F. Llovell, L. F Vega. (2024). *ACS Sustainable Chemistry & Engineering* 12 (31), 11561-11577. DOI: 10.1021/acssuschemeng.4c01961

Ag(II)-based Magnetic Precursors of Novel Superconductors

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Silver(II) is a paramagnetic (4d9) transition metal cation with outstanding oxidizing properties. Its fluoride connections are in many ways analogous to Cu(II) oxides.[1,2] The three key challenges to achieving high-T_C superconductivity in doped Ag(II) fluorides are:

(i) manufacturing a material with flat [AgF_2] layers,
(ii) preparing a mixed-cation material with a strong magnetic superexchange, and
(iii) achieving electronic doping to any of the said materials.

Here we will discuss stoichiometries examined theoretically which contain flat [AgF_2] layers and charge reservoir layers (this should facilitate doping),[3] as well as the first mixed-cation Ag(II)-based fluoride with another paramagnetic TM cation, namely Ag(II)Co(III)F_5.[4] The latter hosts high-spin Co(III) and features strong Ag(II)-Co(III) superexchange interactions via fluoride bridges. We will also present a related Ag(II)Ag(III)F_5 with a rare high-spin Ag(III) and immensely strong superexchange between silver cations of different valences.[5] These advances help to solve problems (i) and (ii) but challenge (iii) is still to be addressed.

Acknowledgement

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References

[1] W. Grochala, R. Hoffmann, Angew. Chem. Int. Ed. Engl., **2001**, 40, 2742.
[2] J. Gawraczyński et al., PNAS, **2019**, 116, 1495.
[3] D. Jezierski, J. Lorenzana, W. Grochala, Phys. Chem. Chem. Phys., **2025**, 27, 2927.
[4] D. Jezierski, Z. Mazej, W. Grochala, Dalton Trans., **2024**, 53, 13731.
[5] D. Jezierski, Ph.D. Thesis, University of Warsaw, **2024**.

Interfacial Molecular Engineering for Functional Materials: New Design Principle for Materials with Permeable Properties

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In this presentation, I will talk about the development of functional material by delicate manipulation of interfacial interactions. Here, the "interface" includes not only the molecular interfaces but also the molecular-solvent interfaces and molecular-electrode interfaces. By this unique strategy, we successfully developed a fluorous nanochannel with ultrahigh water permeability and high desalination capability, by taking advantage of a particular interfacial interaction between fluorous surface and water/ions.[1]

Fluorous nanochannels are constructed by 1D supramolecular assembly of oligoamide macrocycle whose inner lumen is fully fluorinated. Such nanochannels were embedded in the vesicular membrane to measure the water permeability and salt rejection capability. The observed water permeation flux for the nanochannel with an inner diameter of 0.9 nm was 450 times higher than that of aquaporin, a naturally occurring water permeable protein. Moreover, no salt permeation was observed. This is surprising considering that the hydrated diameter of salt (Na^+/Cl^-) is much smaller than the size of the nanochannel. This particular effect is attributed to the effect of the fluorinated surface that can disrupt the hydrogen bonding network of water to facilitate water permeation, while rejecting anions by electrostatic repulsion with negatively charged fluorine atoms.

When we try to develop a desalination membrane with the above-described strategy, a membrane having a high density of continuous pore (pore size ~1 nm) with high mechanical property is required. However, such a membrane is very difficult to obtain, because porous polymers are usually mechanically weak. Very recently, we developed a new method to synthesize crosslinked porous nanomembranes with exceptional mechanical properties by using an electrode interface.[2] We believe this methodology combined with fluorousnanochannel-based molecular design, would lead to the development of next generation desalination membranes.

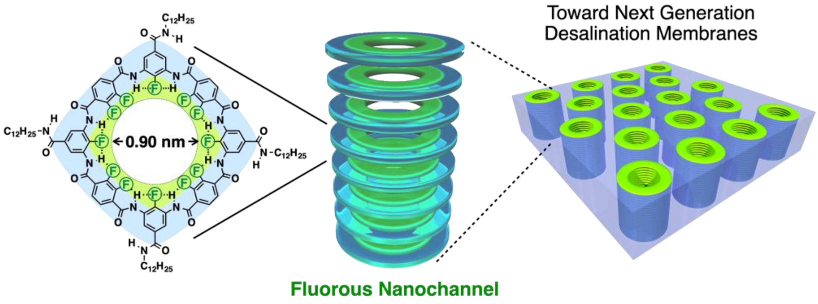

Figure 1. Design of fluorous nanochannel.

References

[1] Y. Itoh, S. Chen, R. Hirahara, T. Konda, T. Aoki, T. Ueda, I. Shimada, J. J. Cannon, C. Shao, J. Shiomi, K. V. Tabata, H. Noji, K. Sato, T. Aida *Science*, **2022**, 376, 738–743.

[2] *Manuscript under revision.*

Exploring Supramolecular Chemistry and Photoredox Catalysis with PFASs and in PFASs

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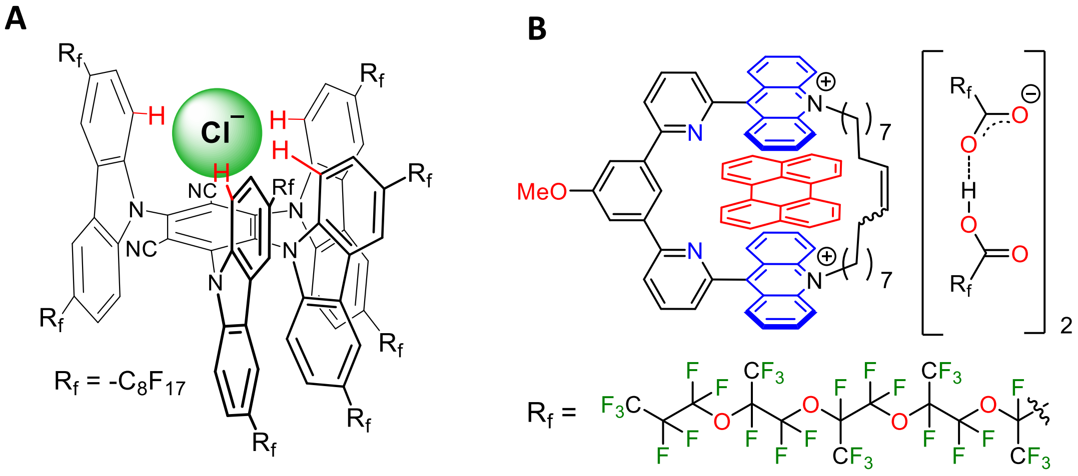
In the presentation, our recent works dealing with the use of highly fluorophilic supramolecular receptors applied to the functionalisation of C(sp^3)–H bonds,[1] to the separation of PAHs (Polyaromatic hydrocarbons),[2] or to drive the self-assembly of unusual radical host-guest complexes, will be described. The benefits of using per-/polyfluoroalkyl substances (PFASs) to improve the efficiency of catalytic and molecular recognition processes will be highlighted.



Scheme 1. Schematic representations of a fluorophilic 4CzIPN chromophore as a host for the chloride anion to form a supramolecular photoredox catalyst for the functionalisation of poorly reactive C(sp^3)–H bonds (**A**),[1] and a highly fluorophilic bis-acridinium cyclophane as a selective host for perylene (**B**).[2]

References

[1] Carré, V.; Godard, P.; Méreau, R.; Jacquot de Rouville, H.-P.; Jonusauskas, G.; McClenaghan, N.; Tassaing T.; Vincent, J.-M. *Angew. Chem. Int. Ed*. **2024**, e2024022964.

[2] Hu, J.; Ward, J. S.; Chaumont, A.; Rissanen, K.; Vincent, J.-M.; Heitz, V.; Jacquot de Rouville H.-P. *Angew. Chem. Int. Ed.* **2020**, *59*, 23206-23212.

Perfluoropolyether-functionalized Carbon-based Materials and their Applications in Energy Devices

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Carbon atoms can arrange to build nanostructures of different dimensionality, shape and properties that are nowadays extensively exploited in many technologies and applications, especially in the field of energy devices (Fig. 1). Even more interestingly, carbon nanomaterials can be efficiently modified with functional molecules, altering their structure and electronic features, broadening the range of properties and widening the fields of their application. In this work, our experience on chemical grafting of perfluoropolyether (PFPE) chains to carbon nanostructures is reviewed and purposed as approach for PFPE covalent functionalization to several carbon-based materials, focusing their application in the field of energy devices [1-3].

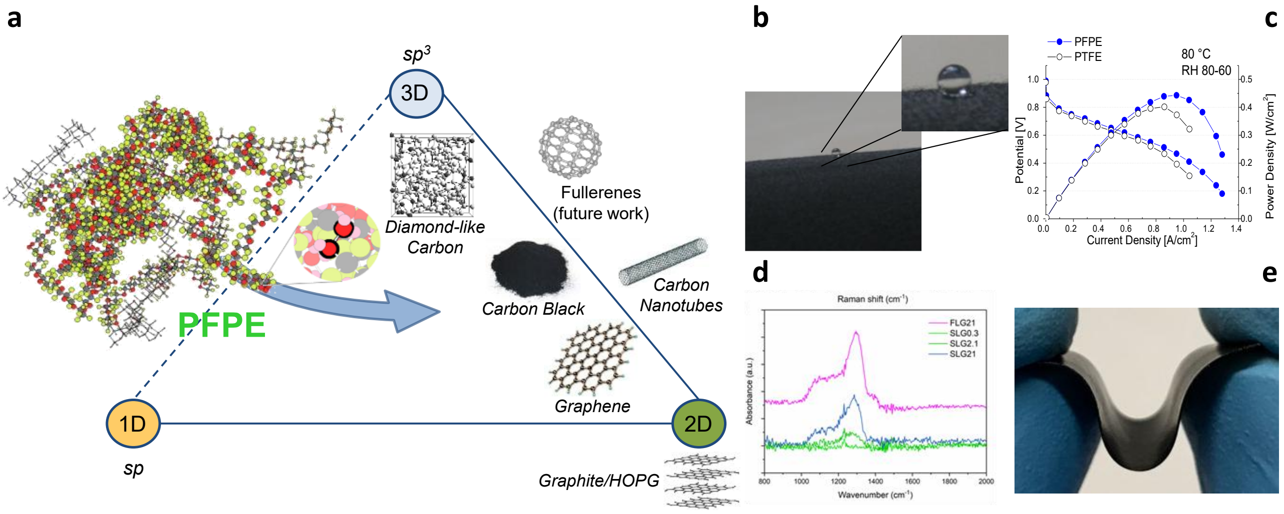

Figure 1. Scheme of (**a**) chemical grafting with PFPE chains to several carbon-based materials; superhydrophpbic PFPE-functionalized carbon cloth (**b**) for GDLs and its polarization curve (**c**) in a PEM-FC; (**d**) FT-IR spectra of PFPE-functionalized graphenes; (**e**) flexible PFPE-functionalized CNTs-based electrode.

References

[1] Sansotera, M.; Marona, V.; Marziani, P.; Dintcheva, N.T.; Morici, E.; Arrigo, R.; Bussetti, G.; Navarrini, W.; Magagnin, L. *Materials*, **2022**, 15(19), 6883.
[2] Gibertini. E.; Gabatel, L.; Lucotti, A.; Bussetti, G.; Bianchi, C.L.; Nobili, L.; Magagnin, L.; Navarrini, W.; Sansotera, S. *Diamond Relat. Mater.*, **2022**, 122, 108810(1-7).
[3] Sansotera, M.; Gola, M.; Dotelli, G.; Navarrini, W. *The Role of Perfluoropolyether in the Development of Polymeric Proton Exchange Membrane Fuel Cells*, Eds: Ameduri, B.; Sawada, H. *RSC Polymer Chemistry Series - Fluorinated Polymers: Volume 2: Applications* (RSC), **2017**, 158-178.

Obtaining Hydrogen Fluoride from Ammonium Polyfluoride in its Interaction with Methane and Oxygen in Burning Mode

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At the moment, the main industrial method of hydrogen fluoride production is the sulfuric acid decomposition of acid-grade natural fluorspar concentrate with sulfuric acid. However, not all countries in the world have CaF_2 reserves. At the same time, the natural reserves of fluorine in the composition of fluorapatite exceed its reserves in the composition of CaF_2 by approximately to 10 times. Fluorine-containing waste from the production of extraction phosphoric acid from $Ca_5(PO_4)_3F$ is mainly disposed of in solid industrial waste landfills. The only technology developed at the industrial level by "BUSS Chem Tech" is characterized by a significant amount of liquid waste [1].

It is known [2] that an effective way to process fluorides to produce HF is their interaction with hydrogen-containing substances and oxygen in combustion mode. The authors have developed a method for processing ammonium polyfluoride, which is obtained by amination of an aqueous solution of hexafluorosilicic acid, the main fluorine-containing by-product of H_3PO_4 production.

Calculations for the groups of elements N-H-F-O and N-H-F-O-C show that in thermodynamically equilibrium mixtures over the entire real range of temperature changes, when the number of hydrogen atoms is greater than or equal to the number of fluorine atoms, the only fluorine-containing substance is HF. Fluorides and oxide-fluorides of nitrogen and carbon, as well as oxygen fluorides, are absent.

Research on the interaction of ammonium polyfluoride with methane and oxygen in combustion mode in a tunnel burner type reactor was carried out at laboratory and pilot-industrial installations. The conditions under which the flame front is stable are determined. The possibility of almost complete regeneration of fluorine from ammonium polyfluoride in the form of HF has been demonstrated.

References

[1] Production of HF from H_2SiF_6 Thomas Dahlke, Olivier Ruffiner, Roderick Cant // Procedia Engineering 138 – December 2016 – p. 231-239 DOI:10.1016/j.proeng.2016.02.080

[2] Production of hydrogen fluoride by the interaction of depleted uranium hexafluoride with methane and oxygen in combustion mode Pashkevich D.S., Zimin A.R., Alekseev Yu. I., Mukhortov D.A., Kambur P.S., Petrov V.B., Bazhenov D.A., Kapustin V.V., Smolkin P.A., Fyodorova T.A. // Journal of engineering physics and thermophysics – 2025 – T. 98. №1. P. 154-163.

Leveraging Molecular Thermodynamics and Machine Learning for the Rational Design of Alternative Refrigerant Blends

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With enforcement of regional and international regulations on limiting F-gases with high global warming potential (GWP), the refrigerant market is in dire need for environmentally benign refrigerants. The development of new synthetic refrigerant molecules is limited by the chemistry of the period table, finding balance between toxicity, flammability, GWP and ozone depletion potential, directing the market towards the development of refrigerant blends. A serious limitation is the large number of refrigerant molecules (natural and synthetic), making their lab-scale development challenges to cover all possible combinations and compositions.

This work introduces a novel, integrated modelling approach combining machine learning, the polar soft-SAFT equation of state (EoS), and process modeling to rationally design binary refrigerant blends. We address the challenge of limited experimental data for parametrizing the polar soft-SAFT EoS by employing machine learning algorithms to predict molecular parameters from COSMO-RS derived molecular descriptors for a diverse set of refrigerants, including HFCs, HFOs, and HCFOs. These predicted parameters are then utilized within the polar soft-SAFT framework to accurately predict thermophysical properties, comparable to results obtained from traditional experimental fitting. Furthermore, we leverage these property predictions complemented with other properties (flammability, toxicity, GWP, ODP), within process models to evaluate the performance of potential binary blends as drop-in replacement for current refrigerants. This integrated methodology facilitates the rapid screening and optimization of new low-GWP refrigerant blends, significantly accelerating the development of sustainable refrigeration technologies by bridging the gap in property data and enabling efficient process design

References

[1] D. J. Weubbles, Int. J. Refrig. ***1994****, 17, 7–17.*
[2] I.I.I. Alkhatib, L.M.C. Pereira, J.Torne, L.F. Vega, Phys. Chem. Chem. Phys., ***2020****, 22, 13171–13191.*
[3] C.G. Albà, C. G.; I.I.I. Alkhatib, F. Llovell, L.F. Vega. ACS Sustain. Chem. Eng. ***2021****, 9, 17034–17048.*

Computational Modeling of the Global Warming Potential Climate Metric Across Fluorinated Molecules

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The impact of hydrofluorocarbons (HFCs) on global warming can be hundreds to thousands of times greater than that of CO_2, with this impact being measured by the Global Warming Potential (GWP), the most widely used emission metric in climate policy, introduced by the Intergovernmental Panel on Climate Change in 1990. With the rapid rise of HFC emissions and their projected catastrophic effects on the atmosphere and climate, the Kigali Amendment [1] of 2016 seeks to drastically reduce the global production and consumption of HFCs, thus contributing to the Paris agreement target of limiting the global temperature rise below 2 degrees Celsius. For this reason, new low-GWP fluorinated compounds are necessary to achieve the Kigali goals and mitigate climate change effectively.

Here, we present our computational approach to the calculation of the GWP, a metric that depends on the atmospheric lifetime and radiative efficiency (RE). The lifetime is calculated with our own cost-effective protocol [2-4] based on multiconformer transition state theory (MC-TST) and a method for performing transition state sampling called constrained transition state randomization (CTSR) [5,6]. The RE is calculated with a new approach where we fit the vibrational frequencies and intensities to obtain RE values with a relative error of only 8% for several classes of fluorinated molecules.

Acknowledgements

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References

[1] Heath E.A. *Int. Leg. Mater.*, **2017**, *56(1)*, 193-205.
[2] Viegas L.P. *J. Phys. Chem. A*, **2021**, *125(21)*, 4499-4512.
[3] Viegas L.P.; Jensen F. *Environ. Sci.: Atmos.*, **2023**, *3(5)*, 855-871.
[4] Viegas L.P. *ChemPhysChem*, **2024**, *24(16)*, e202300259.
[5] Viegas L.P. *Chem. Phys. Lett.*, **2022**, *803*, 139829.
[6] Viegas L.P.; Galvão B.R.L. *Atmos. Environ.*, **2024**, *328*, 120515.

Chiral Fluoroalkylimines in Asymmetric Synthesis: Advances and Applications

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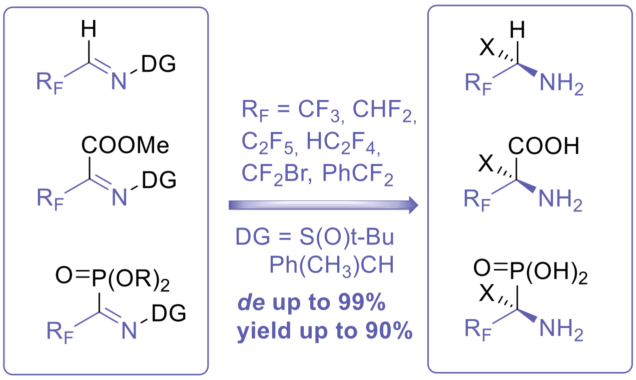
The development of efficient synthetic methods for polyfluoroalkyl amines, α-amino acids, α-aminophosphonic acids, and their derivatives remains a key objective in contemporary organic and bioorganic chemistry. Incorporation of the $CF_3C–N$ structural motif into peptides has led to novel peptidomimetic frameworks with promising biomedical and pharmaceutical potential.[1] [2] The asymmetric synthesis of chiral (poly)fluoroalkylated amino compounds is particularly important, as the biological activity of enantiomers can differ dramatically. Accordingly, the development of reliable strategies for accessing enantiomerically enriched fluorinated amino derivatives represents a significant synthetic challenge.



Fluoroalkylimines bearing stereodirecting groups, such as S(O)t-Bu or $Ph(CH_3)CH$ adjacent to the nitrogen atom, have emerged as versatile substrates for the enantioselective construction of a wide range of acyclic and heterocyclic compounds containing fluorinated amino functionalities. This lecture will highlight recent progress in the asymmetric synthesis of enantiomerically pure fluoroalkylamines and their acyclic and cyclic derivatives, including fluorinated aminocarboxylic and aminophosphonic acids.

References

[1] a) M. Zanda, *New J. Chem*. **2004**, *28*, 1401–1411; b) W. C. Black, C. I. Bayly, D. E. Davis, S. Desmarais, J.-P. Falgueyret, S. Lerger, C. S. Li, F. Masser, D. J. McKay, J. T. Palmer, M. D. Percival, J. Robichaud, N. Tsou, R. Zamboni, *Bioorg. Med. Chem. Lett*. **2005**, *15*, 4741–4744

[2] J. Y. Gauthier, N. Chauret, G. Wesolowski, R. N. Young, R. Zamboni, W. C. Black, *Bioorg. Med. Chem. Lett*. 18, 2008, *18*, 923–928

PARALLEL SESSION IV

Contaminants of Emerging Concern

What do We Know About Per- or Polyfluoroalkyl Substances (PFASs)? Issues, Challenges, Regulations and Possible Alternatives

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Per- or polyfluoroalkyl substances (PFASs)[1-2] are man-made compounds involved in compositions of many industrial processes and consumer products. They are categorized into two main families based on their molar mass: though low molar mass-products (<1000 Da) are toxic, mobile, bioaccumulative and cross the human membranes, others of much higher molar masses, e.g., fluorinated macromolecules and especially fluoropolymers are safe, reliable, do not face such concerns, do not cross the membranes (hence, they are regarded as Polymers of Low Concern)[3] and are involved in many applications including medical products and high value-added materials and devices. Because the former family has led to a severe global contamination, recent regulating agencies in Europe (REACH) and USA (EPA) have aimed at restricting fluorochemicals. Recently, the consultation from affected organisms and industries have led to more than 5,600 answers and comments.[4] This review supplies an update on the overall situation of PFAS,[5] their limitations, regulations, end of life, degradations and possible alternatives.

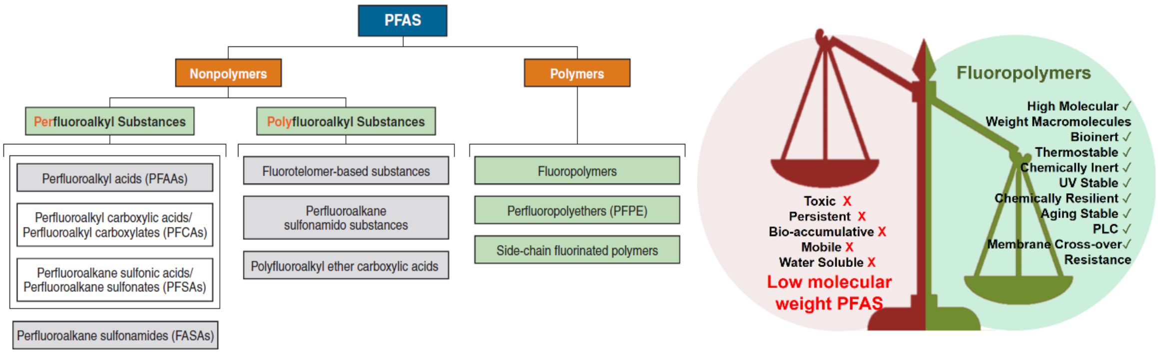

Figure 1: distinguishing PFAS families by their molar masses (MW, left); drawbacks of low MW PFAS in contrast to advantages of high MW ones (Fluoropolymers) (right)

References

[1] R.C. Buck et al., *Integr. Environ. Assess. Manag*., **2011**, 7, 513–541.
[2] B. Améduri, *Perfluoroalkyl substances: Synthesis, Properties and Regulations*, **2022**, RSC, Oxford.
[3] a) B. J. Henry, J. P. Carlin, J.A. Hammerschmidt, R. C. Buck, L. W. Buxton, L. Fiedler, J. Seed, O. Hernandez; *Integr. Environ. Assess. Manag*., **2018**, 14, 316–334; b) S. H. Korzeniowski et al. *Integr. Environ. Assess. Manag*. **2023**, 19, 326-54.
[4] https://www.fia.uk.com/news/echa-received-more-than-5-600-comments-on-the-pfas-restriction-proposal.html (accessed October 6th, 2024).
[5] B. Ameduri, *Macromolecules*, **2025** *(in press; https://doi.org/10.1021/acs.macromol.4c02993)*.

Firefighters’ Occupational Exposure to Per- and Polyfluoroalkyl Substances

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Per- and polyfluoroalkyl substances (PFAS), synthetic forever chemicals used in industries and consumer products due to their resistance to water, grease, and heat, accumulate persistently in the environment and human body [1]. Ubiquitous PFAS pose widespread exposure risks and are linked to endocrine disruption, immune impairment, and cancer [1]. In 2024, the International Agency for Research on Cancer declared perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) as known (Group 1) and possibly (Group 2B) carcinogenic to humans, respectively [2]. As research progresses, regulatory agencies are expected to tighten limits, expand monitoring, and implement phase-out plans for non-essential PFAS uses, particularly in firefighting foams, textiles, and food packaging. Occupationally exposed populations have some of the highest exposures to PFAS, with inhalation as the main exposure route, as well as potential dermal absorption and dust ingestion. Overall, firefighters, industrial workers, and military personnel are at higher risk due to direct contact with PFAS-containing firefighting foams, textiles, and coatings [2]. Moreover, firefighters’ activity is carcinogenic because it causes mesothelioma and bladder cancer, and limited evidence supports the development of colon, prostate, and testicular cancers, melanoma, and non-Hodgkin lymphoma [3]. This work characterizes firefighters’ exposure to PFAS during regular working activities, including structure fire combat and training exercises where firefighting foams have to be used. So far, data on firefighters’ exposure remains scarce, and available information is not representative of the European force of firefighters. Firefighters have elevated exposure levels of certain PFAS compared to the general population and experience latent and cumulative effects of PFAS-containing Aqueous Film-Forming Foams exposure throughout their careers due to firefighting structure (residential/industrial) fires and during training exercises. Available studies will be presented and discussed, accounting for literature data, recommendations/guidelines established by international agencies, and associated health risks.

Acknowledgments

This work received financial support from the PT national funds (FCT/MECI, Fundação para a Ciência e Tecnologia and Ministério da Educação, Ciência e Inovação) through the project UID/50006 - Laboratório Associado para a Química Verde - Tecnologias e Processos Limpos.

References

[1] P.E. Rosenfeld; K.R. Spaeth; L.L. Remy, et al. Env. Research, **2023**, 220, 115164.
[2] IARC Working Group, Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), IARC/WHO, Lyon, France, Vol 135, **2024**, 1-765.
[3] IARC Working Group, Occupational Exposure as a Firefighter, IARC/WHO, Lyon, France, Vol 132, **2023**, 1-730.

Breaking the Chains of PFAS with Electrochemical Oxidation – the SUIKI Bottom-up Approach

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The persistence, bioaccumulation, and toxicity of per- and polyfluoroalkyl substances (PFAS) in water systems present a critical environmental challenge. The removal of PFAS from (waste)water while challenging, is met through use of well-established technologies such as granular activated carbon (GAC), Ion-exchange resins (IXR), nanofiltration (NF) and reverse osmosis (RO) [1]. A burning issue that remains (pun intended) is the disposal of the produced solid or liquid PFAS concentrate, a critical step that must be considered for a holistic PFAS solution, and currently mostly addressed through incineration of spent adsorbent media.

There are several reported destructive technologies for PFAS[2] such as cold plasma, supercritical water oxidation, ultrasonic cavitation, with some alternative ideas emerging recently too, such as piezoelectric ball milling[3]. Electrochemical oxidation stands out as a PFAS destruction method through its unique application style, where electrodes submerged in water are subjected to an electrical potential. This potential dictates together with the electrode materials the type of reactions that are preferential in the aqueous solution. Therefore, through fundamental consideration of material properties via the means of computational and experimental efforts we can tune electrode material properties towards PFAS adsorption and destruction, as well as increase the potential barrier needed for water splitting to occur (through Oxygen and Hydrogen Evolution Reactions a.k.a. OER & HER, respectively), thereby reducing the energy consumption of the treatment system towards water splitting.

Through the direct electron transfer (DET) mechanism between PFAS molecules and the electrodes and by selecting materials with high affinity towards PFAS chemistry, PFAS degradation occurs in a targeted manner (in terms relative to water splitting and degradation of other organic contamination). While in practice achieving absolute preference towards any one group of contaminants is difficult, there are a lot of insights that delving into the fundamentals uncover, and at SUIKI we are collaborating with the material competence center of TDK in Japan to build a portfolio of water treatment electrode materials through fundamental studies in order to destroy PFAS effectively.

First experimental results will be presented with Aqueous Film Forming Foam and Landfill Leachate experiments in bench scale.

References

[1] The U.S. Environmental Protection Agency Office of Research and Development, "Per- and polyfluoroalkyl substances (PFAS) Technologies for Reducing PFAS in Drinking Water." Accessed: Dec. 26, 2024. [Online]. Available: https://www.epa.gov/sites/default/files/2019-10/documents/pfas_drinking_water_treatment_technology_options_fact_sheet_04182019.pdf

[2] S. Verma, R. S. Varma, and M. N. Nadagouda, "Remediation and mineralization processes for per- and polyfluoroalkyl substances (PFAS) in water: A review," *Science of The Total Environment*, vol. 794, p. 148987, Nov. 2021, doi: 10.1016/j.scitotenv.2021.148987.

[3] N. Yang *et al.*, "Solvent-Free Nonthermal Destruction of PFAS Chemicals and PFAS in Sediment by Piezoelectric Ball Milling," *Environ Sci Technol Lett*, vol. 10, no. 2, pp. 198–203, Feb. 2023, doi: 10.1021/acs.estlett.2c00902.

PFAS Degradation During Hazardous Waste Incineration: A Pilot-Scale Study with Comprehensive Analytical Approach

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Context and objectives

PFAS, per- and poly-fluoroalkyl substances, are chemical compounds widely used in industry and everyday consumer products due to their non-stick, waterproof heat-resistant properties. However, these compounds are also resilient and persistent, posing major environmental challenges. Our study aims to evaluate the fate of PFAS during the thermal treatment of real PFAS-contaminated waste (fire-fighting foam AFFF, PFAS saturated adsorbent media,..).

Material and Method

This study was carried out on a R&D pilot unit, designed to reproduce the incineration processes of hazardous waste under controlled conditions. Combustion temperatures (up to 950°C), post-combustion temperatures (up to 1200°C), residence times and other parameters such as flue gas composition (residual O_2% and water content) were set to mimic typical conditions of industrial-scale hazardous waste incineration. An exhaustive and innovative analytical strategy was deployed to monitor PFAS during thermal treatment. The contaminated waste, combustion residues, and fumes were analyzed in LC/MS/MS to determine their content of targeted PFAS (49 substances). The OTM-45 method was particularly used to sample and analyze the gases at emission and thus calculate the destruction and removal efficiency (DRE) of PFAS. Analyses in combustion ionic chromatography (C-IC) were also performed to follow the fluorine (TF, TOF & HF). Finally, additional analyses were conducted in order to identify the presence of products of incomplete combustion (PICs) in the combustion gases. A non-target analysis (NTA) method was developed in liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS) and applied to the analytical fractions of the OTM-45 to identify semi-volatile PICs. Analyses according to the OTM-50 method, by canister sampling and GC/MS analyses, were also implemented to complete these research on very volatile species (like CF4, C2F6,..).

Results and discussion

Tests performed on several matrices showed high degradation of PFAS with DREs reaching up to 99.9999% for POP compounds (PFOS, PFOA, PFHxS). The initial findings from applying non-targeted analysis demonstrate its value by identifying substances that are typically not monitored by targeted analyses. It enables a more comprehensive understanding of the compounds that constitute the TOF, and the combination of these various analytical methods results in a more accurate characterization of PFAS fate during thermal treatment. This study provides crucial data on the effectiveness of thermal treatments for PFAS-containing waste and contributes to developing more efficient management strategies for these persistent pollutants.

Keywords: PFAS analysis, incineration, hazardous waste, destruction efficiency.

PFAS Removal from Landfill Leachates with an Electrochemically Assisted Nanofiltration Membrane

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Leachate from municipal solid waste (MSW) landfills is one main source of PFAS contamination in the environment. Household wastes may contain fluorinated precursors which degrade in the landfill conditions, generating very persistent and very mobile perfluoroalkyl acids (PFAAs). Our own study carried out in four landfill sites located in Spain determined that the Σ_{16}(PFCAs+PFSAs) in raw leachates ranged from 639 ng/L to 1379 ng/L, while in treated leachates was from 856 to 3162 ng/L, the difference explained by the biotransformation of precursor such as flurotelomer alcohols and sulphonamides [1].

This work reports the successful integration of nanofiltration (NF) and electrochemical oxidation (ELOX), and its application to the treatment of landfill leachates. A novelty of the present work is that the two processes were operated in parallel, in contrast to previous studies that reported ELOX alone [2] or treatment trains of NF followed by the ELOX of the NF retentate [3-5]. The experiments were conducted at bench scale, using leachate from a sanitary landfill site. A commercial NF membrane, and an electrochemical cell furnished with boron-doped diamond anodes were working in parallel on the same recirculation tank. The successful continuous operation required of the fine tuning of the process variables, i.e.: the applied current density the pressure in the NF unit, and the feed flowrate. The NF permeate was finely monitored, showing that most PFAS were below the limit of quantification of the analytical method (LC-MS Q-TOF). One major advantage of the proposed integration is the high quality of the permeate water obtained as product of the treated leachate, where secondary electrooxidation products such as fluoride anions were largely rejected.

A major progress is that the proposed integration allows the continuous operation of the system, largely demanded for the upscale of the electrochemical technology where PFAS are not only removed but simultaneously degraded, defluorinated and mineralized.

Acknowledgements

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References

[1] I. Fuentes, S. Gómez-Lavín, M.P. Elizalde, A.M. Urtiaga. *Chemosphere, **2017**, 168, 399-407*.
[2] A. Urtiaga, S. Gomez-Lavin, A. Soriano. *J. Environ. Chem. Eng., **2022**, 10, 107900.*
[3] A. Soriano, E.D. Gorri, A. Urtiaga. *Wat. Res., **2017**, 112, 147-156*.
[4] A. Soriano, C.E. Schaefer, A. Urtiaga. 2020. Enhanced treatment of perfluoroalkyl acids in groundwater by membrane separation and electrochemical oxidation. *Chem. Eng. J. Adv., **2020**, 4, 100042.*
[5] A. Soriano, E.D. Gorri, L. T. Biegler, A. Urtiaga. *Wat. Res., **2019**, 164, 114954.*

Comparison of PFAS contamination Between Two European and Asian rivers

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Poly- and perfluoroalkyl substances (PFAS), have been widely used in aqueous firefighting foam and in various consumer goods, e.g., cookware, food packaging, textiles[1], [2]. However, epidemiological studies have suggested that PFAS can induce cancers, immunotoxic and neurotoxic effects, and a series of health issues [3], [4]. Hence, some PFAS have been listed as priority substances by several regulatory agencies and added as Persistent Organic Pollutants (POPs) by the Stockholm Convention. This study evaluates the contamination of these "forever chemicals" in two river systems: the Garonne River in France and the Red River in Vietnam. The Garonne River flows through highly industrialized, urbanized and agricultural zones before entering the Atlantic Ocean; whereas the Red River, the second largest river in Vietnam, crosses metropolitan Hanoi and plays a crucial role as a freshwater resource and waterway for agriculture and rapidly growing industries. The two rivers are therefore susceptible to PFAS contamination. The analytical approach consisted of i) screening 53 targeted PFAS and ii) applying the Total Oxidizable Precursor Assay (TOPA) in water samples collected at 12 stations along the Red River (06 and 09/2023) and 23 stations along the Garonne River (09/2024). Samples were analyzed by Ultra-High Performance Liquid Chromatography coupled with Mass Spectrometry Orbitrap Exploris$^{\text{TM}}$ 120.

While 21 PFAS were detected in the Red River in June (2.1 to 107 ng.L^{-1}), it was only 13 for September (0.7 to 6.3 ng.L^{-1}). On the other hand, 35 PFAS were quantified in the Garonne River, at much higher levels than those of the Red River (up to 1394 ng.L^{-1}). Perfluoroalkyl acids (PFAA) were the most predominant in both rivers (PFBA, PFBS, PFHxA). PFOA and PFOS levels were well below the European and American regulatory limits, contributing to less than 10% of the PFAS burden in the Vietnamese River. However, concentration of PFOS in the French River exceeded the European quality standard for inland surface water. Besides the legacy PFAAs, emerging PFAS could also be quantified, e.g. fluorotelomer sulfonic acids and sulfonamides, and ether sulfonic acids. TOPA consistently demonstrated higher PFAS levels, implying the presence of non-targeted or unknown PFAS besides the 53 targeted. The elevated PFAS levels in the Garonne River may be associated with Bordeaux and Toulouse airports and historical industrial activities, wastewater effluents, and regulatory gaps in older PFAS use, whereas lower PFAS concentrations in the Red River suggest more recent industrial contributions. The significantly higher discharge rate of the Red River, ranging from 5 to 10 times that of the Garonne River, makes the PFAS flux from both rivers to the sea comparable (t/y).

References

[1] N. Schmidt *et al.*, *Mar Pollut Bull*, **2019**, vol. 149, p. 110491.
[2] M. G. Evich *et al., Science*, **2022**, vol. 375 (no. 6580).
[3] S. E. Fenton *et al.*, *Environ Toxicol Chem*, **2021**, vol. 40 (no. 3), p. 606–630.
[4] S. Kim, I. Thapar, and B. W. Brooks, *Environmental Pollution*, **2021**, vol. 279, p. 116929.

PFAS and Water Resources: How To Determine The Best Treatment Solution?

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Per- and polyfluoroalkyl compounds (PFAS) are a wide range of molecules extraordinarily stable in the environment, making them difficult to treat (especially short-chain PFAS), and also to degrade given their strong chemical structure. The challenges of PFAS treatment are more than fundamental for health, regulatory, technical and economic reasons, and this for all managers and operators of water treatment plants worldwide. The main objective of this study is to provide new solutions for defining the best treatment lines for PFAS in liquid matrices (surface water, groundwater, industrial wastewater, leachates, etc.), with a particular focus on adsorption treatment of short, or even ultra-short chains, which are proving the most difficult to treat.

The study provides new insights into the definition of multi-stage (or non-multi-stage, depending on the situation) adsorption treatment systems, using laboratory-scale experimental methodologies to predict PFAS treatment performance within these systems. These so-called accelerated methodologies, such as that developed by Veolia (Diabolo) or the RSSCT (Rapid Small Scale Column Test), have been evaluated and compared regarding their reliability and robustness to reflect industrial reality.

A comparison of the two lab-scale methodologies for predicting PFAS treatment performance by adsorption showed a very good correlation between them for PFBA (see Figure 1) and the other PFAS. As for the comparison of the latter with the industrial reality using the continuous column pilot unit, the predictions of the PFBA breakthrough curves have an uncertainty evaluated at around 20% for PFBA. Other results for other types of real water matrices used along these comparison tests have shown that the correlation is not obvious, especially between RSSCT predicted breakthrough and industrial reality.

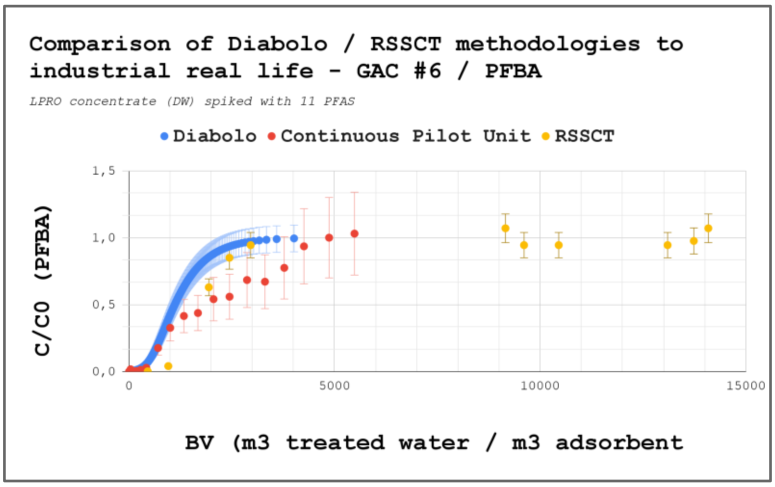

Figure 1. Breakthrough curves of PFBA from Diabolo, RSSCT and industrial pilot unit

Removal of PFAS from Water by Adsorption: Recent Progress and Future Perspectives

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Per- and polyfluoroalkyl substances (PFAS) have gained significant attention due to their extensive occurrence in aquatic environments and their associated toxicity to human health. Adsorption has been considered as an effective remediation technique for achieving increasingly stringent environmental and public health standards for PFAS removal. The current approaches of PFAS adsorption using different adsorbents from drinking water as well as synthetic and actual wastewater are systematically reviewed. Adsorbents with large mesopore volumes and high specific surface areas exhibit enhanced PFAS adsorption kinetics, with optimal adsorption capacities typically observed under low pH conditions. PFAS adsorption mechanisms are mainly electrostatic attraction, hydrophobic interaction, anion exchange, and ligand exchange. Despite the promising adsorption efficiency of various adsorbents, challenges such as low adsorption selectivity, solvent requirement in adsorbents regeneration, and complicated adsorbents preparations should be addressed before large-scale implementation. To facilitate large-scale implementation, decision-support tools such as response surface methodology (RSM), techno-economic assessment (TEA), life cycle assessment (LCA), and multi-criteria decision analysis (MCDA) are discussed in the context of engineering applications. The integration of these analytical frameworks is strongly recommended prior to scale-up to assess the sustainability of future PFAS adsorption process. This critical review provides an in-depth study of the fundamental principles governing PFAS adsorption, offering valuable insights into the development of advanced adsorbents and promoting their practical applicability in large-scale water treatment systems.

PARALLEL SESSION V

Organic and Organometallic Chemistry

Selective Fluorinated Deelectronators and Organometallic Metal-Dimers: A Reactive Couple to Access Unknown Cations

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The heart of our research involves the quest for hitherto unknown cationic entities, that are of interest as textbook examples. For this purpose, we have developed and use a series of heavily fluorinated weakly coordinating anions (WCAs) that we use in conjunction with oligofluorinated fluorobenzene solvents xFB (x = 1-5 consecutive F-atoms) to stabilize the cations in question.[1] In particular, the perfluorinated alkoxyaluminate anions [*pf*]⁻ and [*alfal*]⁻ ([*pf*]⁻ = $[Al(OC(CF_3)_3)_4]^-$; [*alfal*]⁻ = $[F\{Al(OC(CF_3)_3)_3\}_2]^-$), in combination with highly fluorinated solvents like 1,1,1,3,3,3-hexafluoropropane (HFP), 1,2,3,4-tetrafluorobenzene (4FB) or pentafluorobenzene (5FB) led to success.

Apart from halide abstraction, protonation or metathesis reactions, we have in more recent time developed a series of strong, but tuneable fluoroorganic selective deelectronator radical cation salts with potentials vs. Fc^+/Fc spreading between 1.22 and 2.12 V. The use of this fruitful combination for deelectronation of organometallic Transition Metal-Dimers is described in here and routes to a series of unusual complexes, i.e. σ-C-H complexes, H_2-, N_2- and other elemental complexes is presented in the lecture. For the stabilization of the systems relevant for this approach, the three weakly coordinating conditions a-c) in Figure 1 have to met:

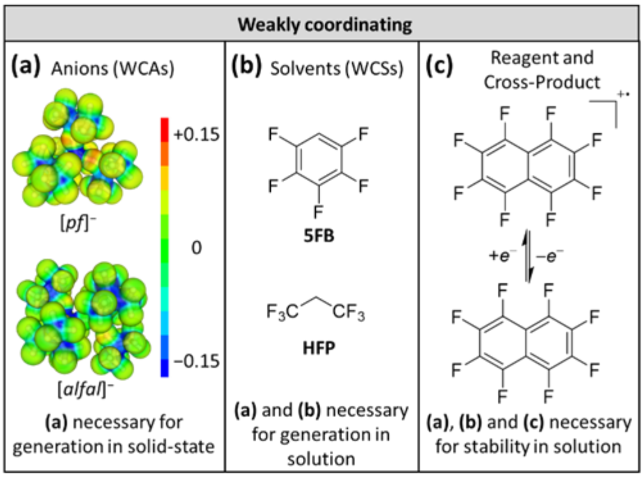

Figure 1. The three mandatory weakly coordinating conditions a-c) relevant to this work.

References

[1] a) Ingo Krossing et al., *Nat. Commun.* **2024**, *15*, 6721. b) Ingo Krossing et al, *Angew. Chem., Int. Ed. Engl.* **2024**, *63*, e202406742.

Dehydrofluorination of Legacy Refrigerants at Group 9 Metal Pincer Complexes

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Here we describe how Group 9 metal pincer complexes could be used to convert high global-warming-potential hydrofluorocarbon refrigerants to fluorinated olefins and beyond. For example, conversion of 1,1,1-trifluoroethane (R-143a) to vinylidine fluoride (VDF) was mediated by the iridium bis(phosphinite) pincer fragment [(POCOP)Ir] (POCOP = 2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$). The reaction at the iridium center is proposed to proceed via a C-H oxidative addition reaction followed by beta-fluoride elimination to afford the metal-bound olefinic product. Crystal structures of a series of hydrofluoroolefins reveal comparative details of metal bonding, and computational analyses and ligand exchange reactions provide insights into the thermodynamics of olefin release.

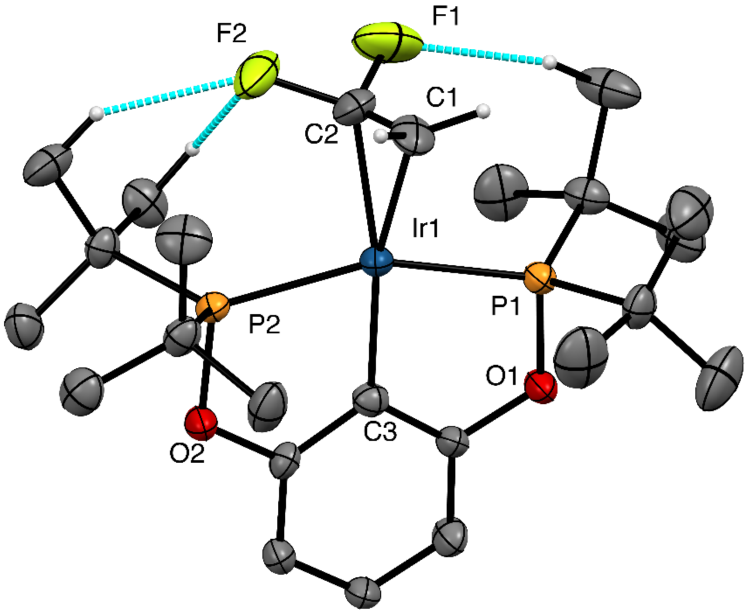

Figure 1. ORTEP diagram of [(POCOP)Ir(VDF)], a product resulting from the functionalization of R-143a. Ellipsoids shown at the 50% level.

Synthetic Reactions of Isolated Trifluoromethyl Isobenzofurans

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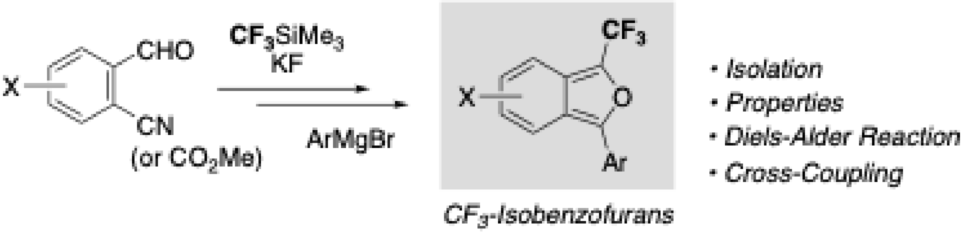
Isobenzofuran has found the use as a reactive diene in Diels-Alder reactions for the construction of polycyclic compounds.[1] Fluorinated isobenzofurans are considered to be promising building blocks for the synthesis of fluorine-containing cyclic systems.[2] We developed a convenient method for the generation of trifluoromethylated isobenzofurans from the precursors (3-trifluoromethyl-1-hydroxyisocoumarans)[3] and their synthetic application. When *o*-cyanobenzaldehyde was treated with CF_3-SiMe in the presence of a catalytic amount of KF, the cascade trifluoromethylation/cyclization proceeded smoothly to give trifluoromethyl phthalides in high yields.[4] Then nucleophilic addition of Grignard reagents (ArMgBr) to ester moieties and the subsequent formation of substituted CF_3-isobenzofurans afforded tetra-substituted naphthalenes via Diels-Alder reactions with various dienophiles such as alkynes. Recently, we succeeded in isolation of trifluoromethyl isobenzofurans as stable compounds. Herein, we present properties and synthetic reactions of the isolated CF_3-isobenzofurans.



Scheme 1. Trifluoromethyl isobenzofurans

References

[1] (a) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1987**, *52*, 2611-2615. (b) Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 4085-4091.

[2] Sakamoto, Y.; Suzuki, T. *J. Org. Chem.* **2017**, *82*, 8111-8116

[3] Komoda, K.; Shimokawa, A.; Amii H. *ChemistrySelect* **2019**, *4*, 2374-2378.

[4] Inaba, M.; Sakai, T.; Shinada, S.; Sugiishi, T.; Nishina, Y.; Shibata, N.; Amii, H. *Beilstein J. Org. Chem.* **2018**, *14*, 182-186.

Reversed Electrostatic Design for Selective Recognition of BTX via π-Hole···π Interactions by a Tetraoxa[2]perfluoroarene[2]triazine Host

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The development of selective molecular recognition systems for industrial hydrocarbon separation is essential for reducing energy losses and minimizing the formation of undesirable side products, contributing to the establishment of a sustainable, low-carbon circular economy. The selective recognition and separation of benzene, toluene, and xylene (BTX) remain significant challenges due to their similar physical properties. In this study, we demonstrate that conventional phenylene-based hosts (π systems, **1–3**) preferentially interact with electron-deficient π-holes, e.g., hexafluorobenzene, rather than electron-rich π systems, e.g., benzene. In contrast, a π-hole-functionalized tetraoxa[2]perfluoroarene[2]triazine (**4**)[1] exhibits an inverse selectivity, favoring benzene via π-hole···π interactions.[2] Investigation of the co-crystallization behavior with BTX resulted in the formation of **4**•2C_6H_6, **4**•0.5(C_7H_8), **4**•0.5(o-C_8H_{10}), **4**•0.5(m-C_8H_{10}), and **4**•2(p-C_8H_{10}), revealing that the triazine ring serves as the primary recognition site. In contrast, p-C_8H_{10} was encapsulated by the tetrafluorophenylene units due to steric hindrance, and among the xylene isomers, only p-C_8H_{10} was reversibly taken up into the crystal. Compared to water, various solvents, and naphthalene, BTX was preferentially included, establishing compound **4** as a non-porous adaptive crystal capable of selectively recognizing BTX and other electron-rich monocyclic aromatic guests. These findings demonstrate its potential for molecular separation applications, highlighting the effectiveness of incorporating perfluorinated aromatic units into host frameworks for enhancing selective molecular recognition.

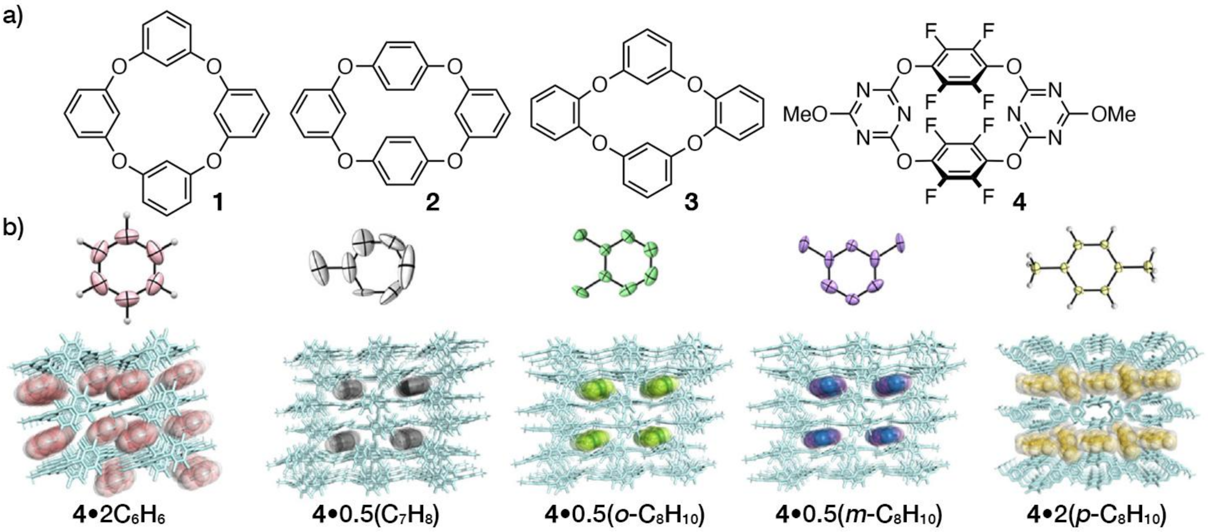

Figure 1. a) Molecular structures of compounds **1-4** and b) Co-crystal structures of BTX with **4**.

References: [1] C. Yang, Y. Chen, D.-X. Wang, L. Zhao, M.-X. Wang, *Organic Lett*. **2013**, *15*, 4414-4417; [2] Y. Ikumura, Y. Habuka, S. Sakai, T. Shinohara, H. Yuge, I. I. Rzeznicka, A. Hori, *Chem. Eur. J.* **2020**, *26*, 5051-5060.

[(Triisopropylsilyl)acetylene]sulfur Pentafluoride – A Valuable Reagent for Accessing Unprecedented Classes of SF_5-Containing Building Blocks

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Herein, we introduce TIPS-CΞC-SF_5 (TASF) as a valuable reagent (liquid, air-stable) that provides access to unprecedented pentafluorosulfanylated structural motifs under benchtop conditions. The versatility of this approach is highlighted by two novel reactions providing convenient and rapid access to the previously undescribed classes of pentafluorosulfanylated enamines or vinyl sulfides.

Our initial work describes the spontaneous addition of secondary aliphatic amines to TASP, providing easy access to the corresponding *(E)*-configured α-SF_5-enamines in good to excellent yields (up to 95%). The reaction tolerates a wide range of functional groups (26 examples) and drug-like molecules. In-silico experiments indicate that the reaction proceeds via a two-step cascade reaction based on initial protodesilylation followed by hydroamination, yielding primarily the *(Z)*-configured zwitter ion that isomerizes via two convergent pathways to yield the *(E)*-configured reaction products. In follow-up work, we found that aromatic as well as primary, secondary and even tertiary aliphatic thiols could be subjected to the corresponding hydrothiolation reaction and form the *(Z)*-β-SF_5-vinyl sulfides in good to excellent yield and *(Z)*-diastereoselectivity under ambient conditions (35 examples, up to 99% yield).

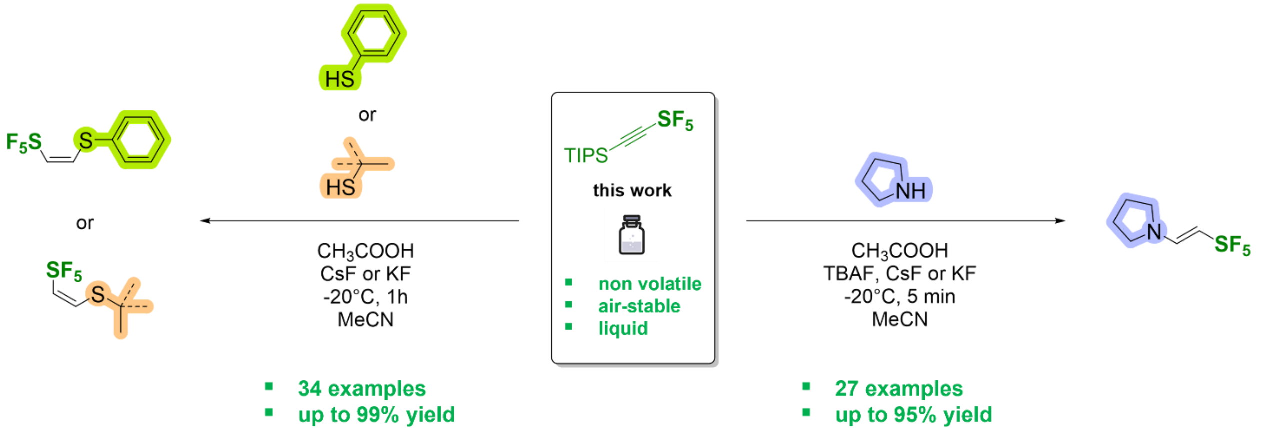

Figure 1. Hydroamination and hydrothiolation of TASP under benchtop conditions.

References

[1] J. O. Wenzel, F. Jester, A. Togni, D. Rombach*, *Chem. Eur. J.* **2024**, 30, e202304015 (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-brg1w).
[2] H. Kucher, J. O. Wenzel, D. Rombach*, *ChemPlusChem* **2024**, 89, e202400168 (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-01jhn).

Unusual Role of Hexafluoroisopropanol in Redox-Activated Cycloadditions

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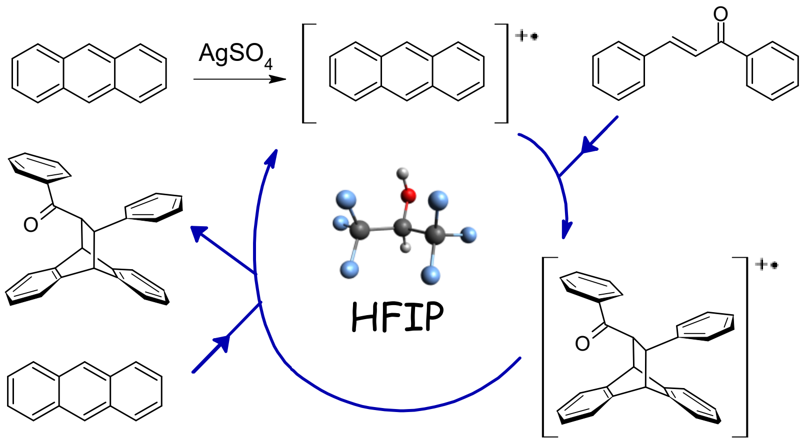
Silver(II) sulfate ($AgSO_4$) is a potent one-electron oxidizer capable of generating aromatic radical cations. Anthracene radical cation readily undergo cycloaddition with chalcone and its derivatives in a catalytic cycle.[1] Our study reveals that hexafluoroisopropanol (HFIP) serves as a unique additive, dramatically enhancing the reaction rate. Even a 1% (v/v) addition of HFIP results in up to a 40-fold increase in cycloaddition efficiency. HFIP as is extensively studied in electrochemistry and organic synthesis due to its unique intermolecular interactions. [2] Our approach combines experiments and theoretical (DFT) calculations, trying to highlight the critical role of HFIP in stabilizing key intermediates and facilitating solvent-substrate interactions. These findings provide new insights into solvent effects in radical cation chemistry and offer a strategy for optimizing oxidative cycloaddition processes.



Scheme 1. Catalytic loop in redox-activated cycloaddition of chalcone to anthracene molecule

References

[1] Jadwiszczak, M. J.; Leszczyński, P.J.; Mazej, Z.; Malinowski, P. J.; Nawrocka, E. K.; Kazimierczuk, K.; Kwiatkowski, P.; Połczyński, P.; Grochowska-Tatarczak, M.; Fijałkowski, K. J.; Sadło J.; Grochala, W. *Org. Chem. Front.,* **2023**,10, 5637-5643.

[2] Caporaletti, F.; Gunkel, L.; Fernández-Ibáñez, M. Á.; Hunger, J.; Woutersen, S. *Angew. Chem. Int. Ed.* **2024**, 63, e202416091

New Access Routes Toward Thiocarbamoyl Fluorides and Trifluoromethanesulfenamides Using an Easy-to-use and Shelf-stable CF_3S-Reagent

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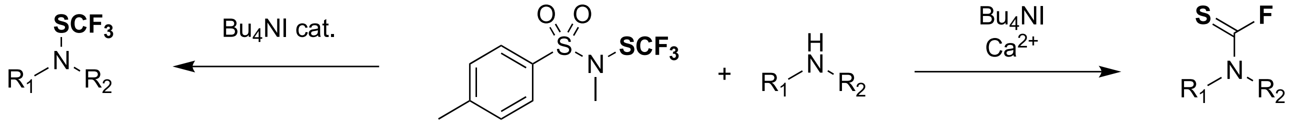
In recent years, fluorine chemistry has taken on an increasingly important role in scientific research, thanks in particular to the special properties of the fluorine atom [1], and this element now plays a key role in medicinal chemistry in particular [2]. Consequently, the search for new ways of accessing fluorinated motifs, combining fluorine with other heteroatoms in particular, is a very dynamic area of research.

As part of this research, we have developed new ways of accessing thiocarbamoyl fluorides [3] and trifluoromethanesulfenamides [4], taking advantage of the great reactive versatility of the "BB23" reagent developed by our team [5]. We discovered that, starting from the same amine, the amount of iodide and the presence or absence of Ca^{2+} allowed us to selectively obtain the thiocarbamoyl fluoride or the trifluoromethanesulfenamide compound. With the development of this new and easy pathway toward thiocarbamoyl fluorides, the properties of these compounds were also studied.



BB23

Scheme 1. New access routes towards thiocarbamoyl fluorides and trifluoromethanesulfenamides

References

[1] a) N. A. Meanwell, *J. Med. Chem.* **2018**, *61*, 5822-5880; b) A. Leo, C. Hansch, D. Elkins, *Chem. Rev.* **1971**, *71*, 525-616.

[2] a) C. Zhang, K. Yan, C. Fu, H. Peng, C. J. Hawker, A. K. Whittaker, *Chem Rev* **2022**, *122*, 167-208; b) Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai, N. Shibata, *iScience* **2020**, *23*, 101467; c) M. Inoue, Y. Sumii, N. Shibata, *ACS Omega* **2020**, *5*, 10633-10640.

[3] C. Delobel, E. Chefdeville, F. Toulgoat, T. Billard, *Adv. Synth. Catal.* **2024**, *366*, 3474-3480.

[4] C. Delobel, F. Toulgoat, T. Billard, *J. Fluorine Chem.* **2024**, *279*, 110353.

[5] a) F. Toulgoat, F. Liger, T. Billard, in *Organofluorine Chemistry: Synthesis, Modeling, and Applications* (Eds: K. Szabó, N. Selander), Wiley-VCH, Weinheim, Germany, **2021**, pp. 49-97; b) Q. Glenadel, M. Bordy, S. Alazet, A. Tlili, T. Billard, *Asian J. Org. Chem.* **2016**, *5*, 428-433.

A New Sulfoximine Scaffold for the Generation of Diverse Fluorinated Radicals in Photoredox Catalysis

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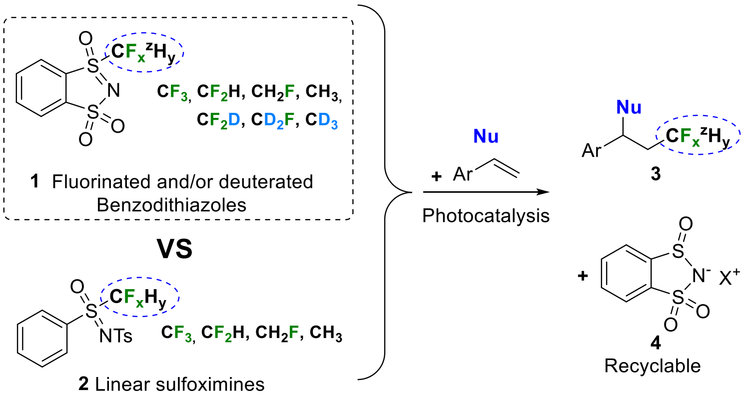
Fluoroalkylated sulfoximines are significantly involved in the numerous advances in fluoromethylation made recently, as electrophiles and radical donors. We can cite the work of Shibata, [1], Hu [2] and Akita [3] in this field. Scarce examples of deuterofluoromethylation are also found in literature. [4] Our group has contributed to these advances, [6] focusing in particular on cyclized fluorinated sulfoximines inspired by the work of Adachi and Ishihara. [7] An efficient synthetic route to these sulfoximines **1**, analogues of benzodithiazoles with -CF_xH_y groups, has been developed. [8]
We will present optimized scale-up syntheses of these benzodithiazoles, essential for their use as reagents. Their radical reactivities in photoredox catalysis **3** and a comparison with their linear counterparts **2** will be discussed, highlighting the advantages of this new structure over more conventional sulfoximines. Moreover, easy deuteration of these benzodithiazoles allows them not only to react as •CF_xH_y donors (from •CF_3 to •CH_3), but also as •CF_xD_y donors, forming unique functional groups. We will finally demonstrate how these molecules can be used in flow chemistry and recycled after use **4**, making them even more promising tools.



Scheme 1. Use of Cyclic Sulfoximines as (Deutero)(fluoro)methylation Reagents.

References

[1] Noritake, S.; Shibata, N.; Nakamura, S.; Toru, T.; Shiro, M. *Eur. J. Org. Chem*. **2008**, 3465-3468.
[2] Zhang, W.; Wang, F.; Hu, J. et al. *Org. Lett*. **2009**, 11, (10), 2109-2112.
[4] Noto, N.; Koike, T.; Akita, M. et al. *ACS Catal*. **2019**, 9, (5), 4382-4387.
[5] Liang, J.; Wang, G.; Dong, L.; Pang, X.; Qin, J.; Xu, X.; Shao, X.; Li, Z. *Org. Lett.* **2021**, 23, (14), 5545-5548.
[6] Pégot, B.; Urban, C.; Bourne, A.; Le, T. N.; Bouet, S.; Marrot, J.; Diter, P.; Magnier, E. *Eur. J. Org. Chem*. **2015**, 3069.
[7] Adachi, K., Ishihara, S. *Japan Tokkyo Kokai Patent*, **2005,** 145917.
[8] Duhail, T.; Messaoudi, S.; Dagousset, G.; Marrot, J.; André-Barrès, C.; Magnier, E.; Anselmi, E. *Adv. Synth.Catal.* **2023**, 365, 2392-2399.

Stereoselective Synthesis of (2*S*,4*S*)-5,5,5,5’,5’-Pentafluoroleucine and (2*S*,4*R*)-5,5,5-Trifluoroleucine

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Keywords: Stereoselective synthesis; fluorinated amino acids; hydrogenation; hydrodefluorination

Fluorinated amino acids are privileged structural motifs in various fields such as medicinal chemistry, chemical biology and supramolecular chemistry.[1–3] Amino acids with polyfluorinated side chain have emerged as promising building blocks to modulate the properties of bioactive peptides,[1] and have proved particularly well-suited to study the structure and function of proteins using ^{19}F NMR.[4] Leucine is the most frequently found in the hydrophobic core of proteins and is also found in many therapeutic peptides. Polyfluorinated leucines are thus highly appealing for biological applications. Adjusting the position and the number of fluorine atoms incorporated is critical to fine-tune the volume, polarity and hydrophobicity of the isobutyl side chain,[5] which can significantly impact biological properties.[6] This modulation can also greatly change the ^{19}F NMR chemical shifts, helping to minimize fluorine signal overlaps, e.g. when multiple fluoroleucine residues are incorporated in protein.[7]

We recently developed a straightforward route to synthesize both (*S*)- and (*R*)-5,5,5,5’,5’,5’-hexafluoroleucine based on a stereoselective fluoroalkylation.[8,9] However, synthesizing fluoroleucine with an unsymmetrical partially fluorinated side chain in a stereoselective manner remains highly challenging due to the creation of an additional chiral center. In this communication, we will present the stereoselective synthesis of two challenging amino acids, (2*S*,4*S*)-5,5,5,5’,5’-pentafluoroleucine, a novel amino acid, and (2*S*,4*R*)-5,5,5-trifluoroleucine (Fig 1) via the stereoselective hydrogenation and hydrodefluorination reactions.[10]

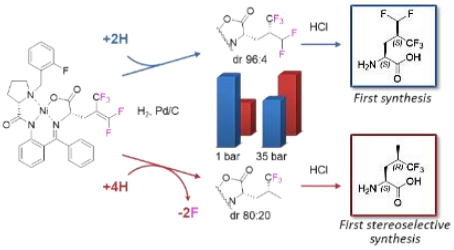

Figure 1. Structures of (2*S*,4*S*)-5,5,5,5’,5’-pentafluoroleucine and (2*S*,4*R*)-5,5,5-trifluoroleucine

References

1. H. Mei, J. Han, K. D. Klika, K. Izawa, T. Sato, N. A. Meanwell, V. A. Soloshonok, *Eur. J. Med. Chem.* **2020**, *186*, 111826.
2. M. A. Miller, E. M. Sletten, *ChemBioChem* **2020**, *21*(24), 3451.
3. E. N. G. Marsh, *Acc. Chem. Res.* **2014**, *47*(10), 2878.
4. I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology* **2009**, 213.
5. A. A. Berger, J.-S. Völler, N. Budisa, B. Koksch, *Acc. Chem. Res.* **2017**, *50*, 2093–2103.
6. J. Y. Gauthier, N. Chauret, W. Cromlish, S. Desmarais, L. T. Duong, J.-P. Falgueyret, D. B. Kimmel, S. Lamontagne, S. Léger, T. LeRiche et al., *Bioorg. Med. Chem. Lett.* **2008**, *18*, 923–928.
7. A. Maleckis, E. H. Abdelkader, I. D. Herath, G. Otting, *Org. Biomol. Chem.* **2022**, *20*, 2424–2432.
8. A. Delamare, G. Naulet, B. Kauffmann, G. Guichard, G. Compain, *Chem. Sci.* **2022**, *13*, 9507.
9. G. Naulet, A. Delamare, G. Guichard, G. Compain, *Eur. J. Org. Chem.* **2023**, e202201148.
10. S. Mummadi, B. Kauffmann, G. Guichard, G. Compain, *Manuscript under preparation.*

Enantioselective Construction of a Fluorinated Tertiary Carbon Using Primary Amine Catalysts

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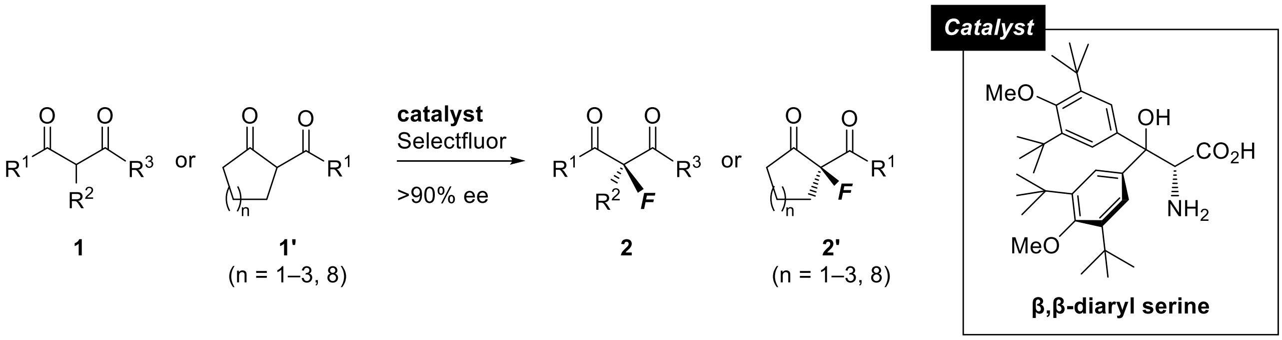
It is well-established that organofluorine compounds play a pivotal role in medicinal chemistry. Among the vast array of fluorinated bioactive molecules, fluorinated tertiary carbons represent some of the most challenging motifs within the realm of fluorinated sp^3 carbons [1]. Therefore, numerous catalytic strategies have been developed to construct these complex structures.

Enamine catalysis has emerged as a promising approach for asymmetric fluorination; however, significant limitations persist regarding both the scope of carbonyl substrates amenable to such transformations and the overall catalytic efficiency. Our research group has recently developed β,β-diaryl serines as novel primary amino acid catalysts, demonstrating their ability to construct fluorinated tertiary carbons on both acyclic and cyclic α-substituted β-diketones with outstanding enantioselectivity (>90% ee) [2,3].
In this presentation, we will discuss the details of these enantioselective fluorination methodologies using β,β-diaryl serine catalysts and explore their synthetic applications.



Scheme 1. β,β-diaryl serine catalyzed fluorination of α-substituted β-diketones

References

[1] Zhu, Y.; Han, J.; Wang, J.; Shibata, N.; Sodeoka, M.; Soloshonok, V. A.; Coelho, J. A. S.; Toste, F. D. *Chem. Rev.* **2018**, *118* (7), 3887–3964.
[2] Poorsadeghi, S.; Endo, K.; Arimitsu, S. *Org. Lett.* **2022**, *24* (1), 420–424.
[3] Endo, K.; Tomon, D.; Arimitsu, S. *J. Org. Chem.* **2023**, *88* (13), 9037–9045.

PARALLEL SESSION V

Organic Chemistry

Upgrading the Halogen Bond donor ability of Organic Fluoroarenes

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The halogen bond is the attractive interaction wherein halogens accept electron density (namely act as electrophiles) from electron rich partners (which acts as nucleophiles). Fluorine has a remarkably weak tendency to form this type of interactions.[1] It will be shown that η^6-coordination of $Cr(CO)_3$ to fluoroarenes increases significantly the electrophilicity of the halogen, enabling the formation of halogen bonds (Figure 1). It will be also reported that η^6-coordination of $Cr(CO)_3$ to substituted arenes increases the electrophilicity of several other heteroatoms appended to the arene.

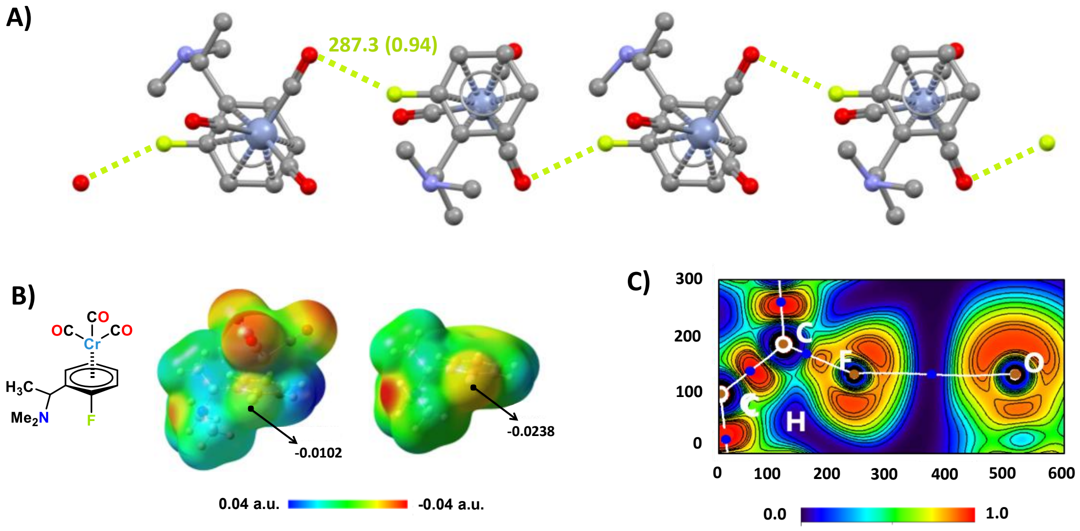

Figure 1. A: Representation of the supramolecular infinite chain formed in the solid by [(1-fluoro-2-(1-dimethylaminoethyl)benzene]chromium tricarbonyl (**1**) via F···O halogen bonds, the interaction length is given in pm, the normalized contact in parenthesis. B: structural formula of compound **1** (left); MEP surfaces (isovalue at density 0.001 a.u.) for complex **1** (mid) and for corresponding non-complexed arene (right). Black dots indicate positions of maximum potential (values in a.u.). C: Distribution of ELF in C–F···O plane of **1** dimers; bond paths are white lines, electron density (3, -1) CPs are blue dots, (3, - 3) CPs brown dots.

References

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, *116*, 2478−2601.

A. Dhaka, R. Beccaria, A. Pizzi, E. Yu. Tupikina, V. Yu. Kukushkin, G. Resnati, *Chem. Eur. J.* **2025**, *31*, e202404570.

Catalyst Free O-Arylation Reactions of Fluorobenzenes

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Arylation reactions of heteroatoms are essential organic chemical transformations. Commonly, these are carried out through transition-metal catalyzed cross coupling reactions. Albeit, cross couplings have some drawbacks as these are costly, oxygen sensitive and may leave toxic metal contaminants in the products. As an alternative, we have explored catalyst-free arylation by S_NAr reactions of fluorobenzene derivatives [1] with regard to scope, mechanism and applications [2,3,4,5]. Here we present our recent results of exploring reactivity, selectivity and scope of these reactions when applying O-nucleophiles. This includes applying a broad range of substrates including natural products, using ^{19}F-NMR spectroscopy for mapping reactivity and producing new types of polymers.

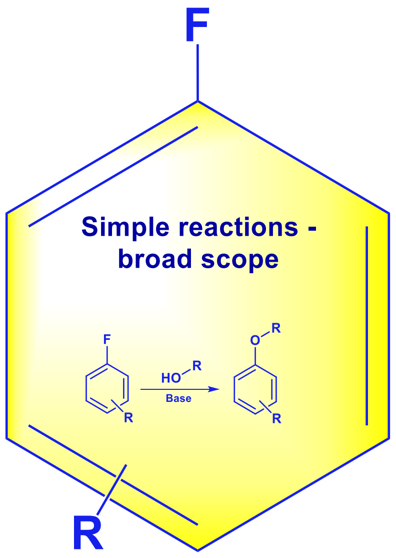

Figure 1. Principle of O-arylation through SNAr reaction of fluorobenzenes.

References

[1].H. Amii, K. Uneyama, Chem. Rev. 2009, 106, 2119
[2].F. Diness, D. P. Fairlie, Angew. Chem. Int. Ed. 2012, 51, 8012
[3].F. Diness, M. Begtrup, Org. Lett. 2014, 16, 3130
[4].C B. Jacobsen, M. Meldal, F. Diness, Chem. Eur. J. 2017, 23, 846
[5].A. M. Embaby, S. Schoffelen, C. Kofoed, M. Meldal, F. Diness, Angew. Chem. Int. Ed. 2018, 57, 8022

Activation of Aromatic Carbon–Fluorine Bonds: Coupling Reaction of Fluorobenzofurans

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*Kohei Fuchibe,[2] Junji Ichikawa,[3,]**

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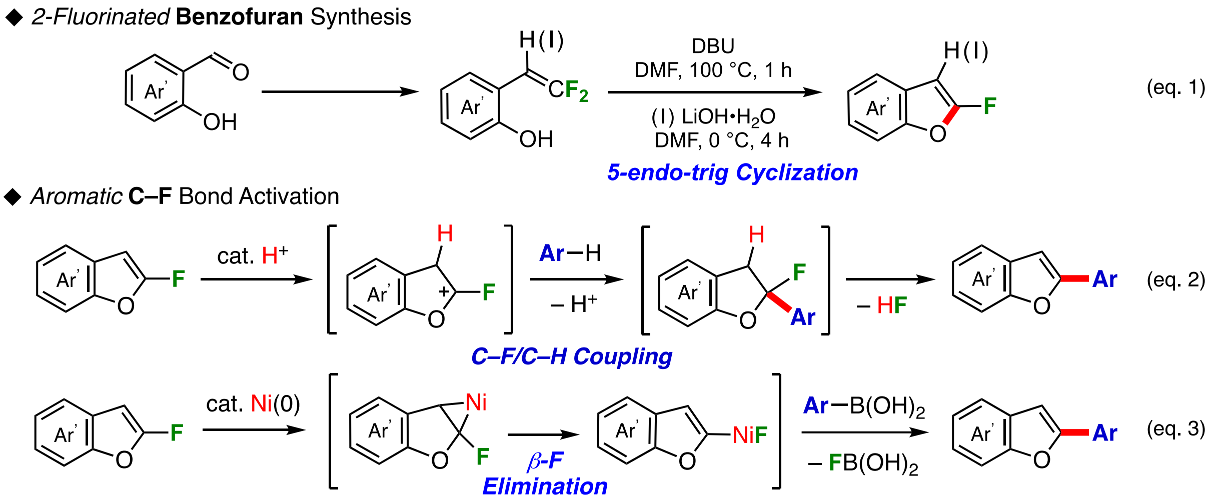
Compounds with a benzofuran skeleton serve as pharmaceuticals, agrochemicals, and functional materials. Some natural products containing a benzofuran ring arylated at the 2-position exhibit biological activities, such as anti-inflammatory effects. While introducing an aryl group into 2-halobenzofurans via oxidative addition to transition metals is effective, it often necessitates heating or special directing groups and/or ligands to convert C–Br and C–I bonds. We previously established and recently improved a simple synthetic method for 2-fluorobenzofurans. However, activating the C–F bond in benzofurans still remains challenging, with limited reported examples. To address this issue, we developed novel methods for C–F bond activation that do not depend on oxidative addition, thereby facilitating the synthesis of 2-arylbenzofurans.
This paper first presents our synthetic method for 2-fluorobenzofurans (eq. 1),[1] followed by a discussion of coupling reactions based on cation formation by *proton* (eq. 2)[2,3] and metallacycle formation by *Ni(0)* (eq. 3),[4] both of which proceed under mild conditions.



References
[1] Morioka, R.; Fujita, T.; Ichikawa, J. *Helv. Chim. Acta* **2020**, *103*, e2000159.
[2] Fujita, T.; Morioka, R.; Fukuda, T.; Suzuki, N.; Ichikawa, J. *Chem. Commun.* **2021**, *57*, 8500–8503.
[3] Fujita, T.; Fukuda, T.; Suzuki, N.; Ichikawa, J. *Eur. J. Org. Chem.* **2022**, *37*, e202201015.
[4] Fujita, T.; Yabuki, H.; Morioka, R.; Fuchibe, K.; Ichikawa, J. *Beilstein J. Org. Chem.* **2025**, *21*, 146–154.

Polyfluoroalkoxylation of Diaryliodonium Salts via Eliminative Ligand Coupling Using Polyfluoroalkoxy Borate Salts

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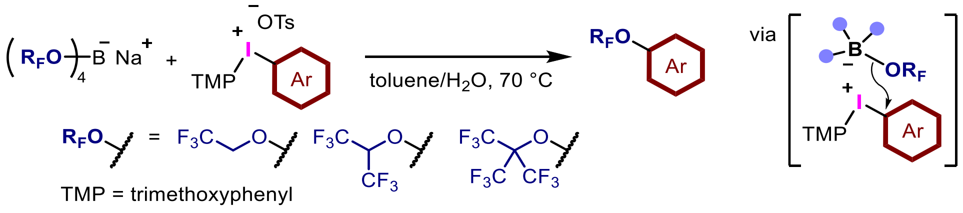
Fluoroalkoxy groups, such as trifluoroethoxy, are commonly found in pharmaceuticals and agrochemicals. The replacement of nonfluorinated alkoxy groups in bioactive compounds with their fluorinated counterparts leads to changes in lipophilicity. With the growing recognition of polyfluorinated alkoxy groups in drug design, the development of efficient synthetic methods for these motifs has attracted considerable attention.

Trifluoroethyl aryl ethers are traditionally synthesized via the Williamson ether synthesis using trifluoroethoxy sources with strong leaving groups or via nucleophilic aromatic substitution (S_NAr) of highly electron-deficient arenes.[1] Transition metal-catalyzed coupling reactions offer broader substrate scope, although these have some drawbacks, such as high cost and toxicity. As a metal-free alternative, ligand coupling of diaryliodonium salts with fluoroalkoxy nucleophiles has emerged as an efficient strategy.[2] However, existing methods required strong bases, such as NaH or $LiN(SiMe_3)_2$, which limited substrate compatibility.

Herein, we report an additive-free polyfluoroalkoxylation of diaryliodonium salts. The reaction of aryl(trimethoxyphenyl)iodonium tosylates[3] with tetrakis(trifluoroethoxy)borate in a biphasic toluene–water system (4:1) at 70 °C afforded trifluoroethyl aryl ethers in moderate to high yields.[4] This protocol exhibits broad functional group tolerance, effectively incorporating both electron-deficient and electron-donating substituents, and enables the synthesis of diverse polyfluoroalkyl aryl ethers (Scheme 1). NMR monitoring indicates that ligand exchange initially forms iodonium borate, which then undergoes intramolecular polyfluoroalkoxy transfer to the aryl group, resulting in the desired product with borate elimination.



Scheme 1. Polyfluoroalkoxylation of aryl(trimethoxyphenyl)iodonium salt using polyfluoroalkoxy borate.

References

[1] Pethő, B.; Novák, Z. *Asian J. Org. Chem.*, **2019**, *8*, 568.
[2] (a) Sundalam, S. K.; Stuart, D. R. *J. Org. Chem.*, **2015**, *80*, 6456; (b) Lindstedt, E.; Stridfeldt, E.; Olofsson, B. *Org. Lett.*, **2016**, *18*, 4234; (c) Gallagher, R. T.; Jha, S.; Metze, B. E.; Stuart, D. R. *Synlett*, **2024**, 889.
[3] (a) Kikushima, K.; Yamada, K.; Umekawa, N.; Yoshio, N.; Kita, Y.; Dohi, T. *Green Chem.*, **2023**, *25*, 1790; (b) Kikushima, K.; Komiyama, K.; Umekawa, N.; Yamada, K.; Kita, Y.; Dohi, T. *Org. Lett.*, **2024**, *26*, 5347; (c) Dohi, T.; Elboray, E. E.; Kikushima, K.; Morimoto, K.; Kita, Y. *Chem. Rev.*, **2025**, in press. DOI: 10.1021/acs.chemrev.4c00808
[4] Kikushima, K.; Tsuda, T.; Miyamoto, N.; Kita, Y.; Dohi, T. *Chem. Comm.*, **2024**, *60*, 10552

Selective C(sp^3)–F Bond Functionalization of Trifluoromethyl Arenes Utilizing EDA Complex

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Mono-selective C–F bond functionalization of trifluoromethyl moiety provides useful strategy for the construction of difluoromethylated compounds, which are bioisostere of ethers and ketones.$^{1)}$ We have developed an electron-donor-acceptor (EDA) complex mediated single-electron transfer of α,α,α-trifluoromethyl arenes in the presence of lithium salt to give α,α-difluoroalkyl arenes (Figure 1). We propose to call this phenomenon fluoride-coupled electron transfer (FCET). On treatment of trifluoromethyl arenes and α-methylstyrene derivatives in the presence of lithium iodide and triethylamine under photo-irradiation, monoselective C–F bond reduction proceeded to generate radical intermediate, which reacted with α-methylstyrenes to furnish α,α-difluorinated γ-alkenyl arenes in good yields. Allylstannanes also participated in the reaction to furnish α-allylated α,α-difluoroarenes. (Scheme 1)$^{2)}$

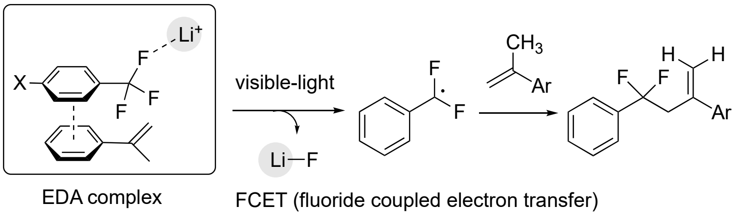
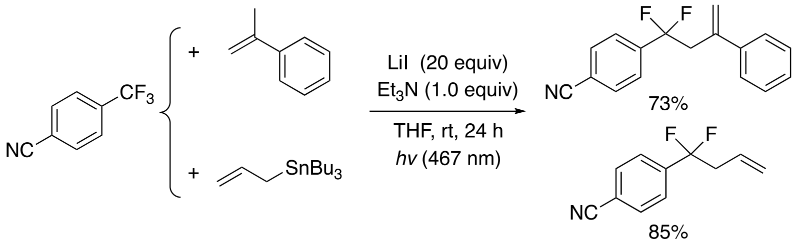


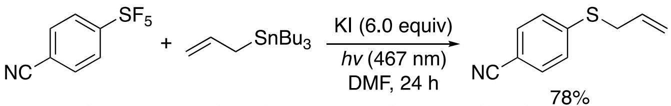
Figure 1. Use of EDA complex for the SET



Scheme 1. Mono-selective C–F bond functionalization of α,α,α-trifluoromethyl arenes.

We will also discuss on the C–F bond functionalization of α,α,α-trifluoromethyl styrenes using the EDA complex.

We also investigated S–F bond activation of pentasulfanyl arenes with allyltributylstannane in the presence of KI under the photoirradiation to give allyl sulfides in good yields (Scheme 2).$^{3)}$



Scheme 2. S–F bond activation of pentasulfanyl arene.

References

[1] For a review: Roy, S.; Besset, T. *JACS Au* **2025**. DOI: 10.1021/jacsau.4c01158.
[2] Uchikura, T.; Akutsu, F.; Tani, H.; Akiyama, T., *Chem. Eur. J.,* **2024**, *30*, e202400658.
[3] Uchikura, T.; Akutsu, Akiyama, T., submitted.

Functional Group Transformation at C5 Position of Fluorinated Isoxazolines via C-F Bond Cleavage.

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To develop fluorinated heterocyclic systems as important pharmacophores, we successfully introduced -OR, -NR$_2$, and -SR groups at the C5 position of 4,4,5-trifluorinated isoxazolines (**3**), which were derived from the corresponding isoxazoles (**1** or **2**) [1-3]. This reaction would proceed via the S$_N$1 mechanism, involving a carbocation intermediate formed by the cleavage of the C-F bond. Additionally, The fluorine atom on C5 position of **3** could also be transformed to aryl and heteroaryl groups via the S$_E$Ar mechanism.[4] Here, we will show the variations with other carbon nucleophiles, including our previous results.

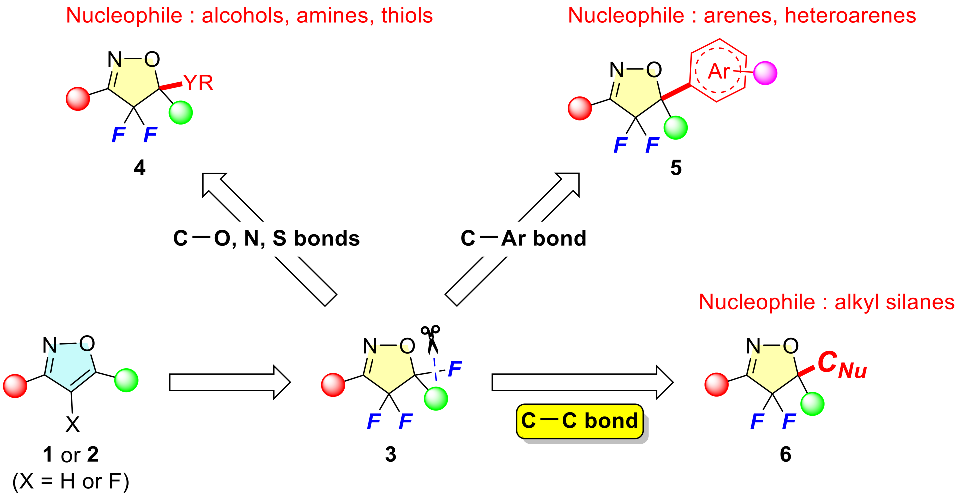

Figure 1. Functional group transformation at C5 position of fluorinated isoxazolines via C-F bond cleavage.

References

[1] Sato, K.; Sandford, G.; Shimizu, K.; Akiyama, S.; Lancashire, M. J.; Yufit, D. S.; Tarui, A.; Omote, M.; Kumadaki, I.; Harusawa, S.; Ando, A. *Tetrahedron*, **2016**, *72*, 1690–1698.
[2] Sato K.; Sandford G.; Konishi Y.; Yanada N.; Toda C.; Tarui A.; Omote M. *Org. Biomol. Chem.*, **2019**, *17*, 2818–2823.
[3] Sato, K.; Nakano, K.; Ueda, T.; Kitamura, Y.; Tanaka, Y.; Karuo, Y.; Tarui, A.; Kawai, K.; Omote, M. *J. Fluorine Chem.*, **2024**, *279*, 110335.
[4] Sato, K.; Kuroki, T.; Minami, H.; Sato, A.; Karuo, Y.; Tarui A.; Kawai, K.; Omote M. *RSC Adv.*, **2024**, *14*, 39543–39549.

Photoacid-Induced Addition of Ketene Silyl Acetals to Fluorinated Isocoumarins and Defluorinative Ring Rearrangement of the Adducts

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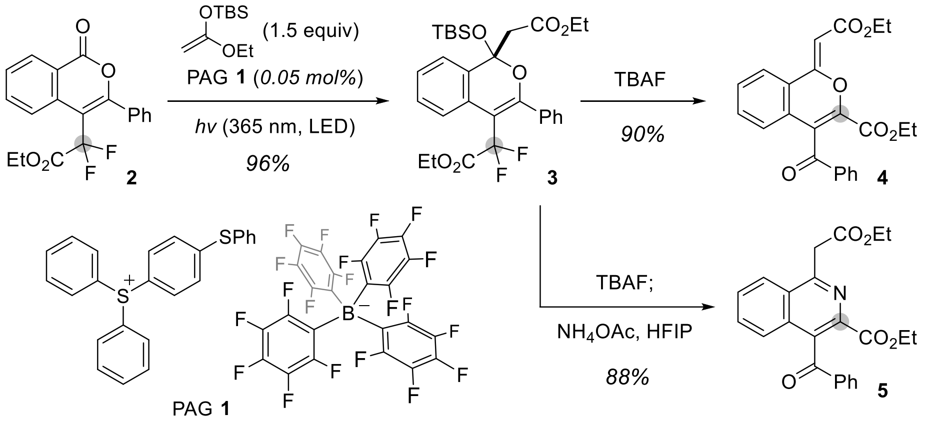
Despite rich applications of photoacid generators (PAGs) in polymer science such as photoresists or photopolymerization initiators, their use in organic synthesis has been still limited. On the other hand, we have found that triarylsulfonium-based PAGs are highly effective pre-catalysts for the Mukaiyama aldol chemistry. For example, in the presence of only 0.05 mol% of commercially available triarylsulfonium salt **1**, the reaction of isocoumarin **2**, bearing a difluoroacetate moiety at the C4 position, with a ketene silyl acetal under UV light irradiation gave not the corresponding substitution product but the *adduct* **3** (Scheme 1). During this molecular transformation, relatively more electron-deficient carbonyl group of the difluoroacetate moiety was totally tolerated. The role of the counter anion in PAGs was critical, especially triarylsulfonium salts containing less-coordinating anions such as tris(pentafluorophenyl)borate showed sufficient (pre)catalyst performance. The lactol silyl ether thereby obtained can be regarded as a stable and isolatable equivalent of the tetrahedral intermediate in the nucleophilic acyl substitution reaction.[1] Indeed, the subsequent treatment with tetrabutylammonium fluoride (TBAF) enabled a unique ring-rearrangement reaction; the formation of divinyl ether **4** involving double C-F cleavage. Similarly, a sequential treatment of **3** with TBAF and ammonium acetate yielded isoquinoline **5** in a one-pot manner. The details will be presented in my talk.



Scheme 1. Photoacid-induced addition of KSA to isocoumarin **2** and transformations of adduct **3**

References [1] H. Yanai, B. Witulski, T. Matsumoto et al. *Chem. Eur. J.* **2024**, *30*, e202401965; H. Yanai, K. Funabiki, T. Matsumoto et al. *Chem. Eur. J.* **2023**, *29*, e202301703; H. Yanai, B. Witulski, T. Matsumoto et al. *Chem. Eur. J.* **2021**, *27*, 11442; H. Yanai, T. Matsumoto et al. *Chem. Commun.* **2016**, *52*, 7974.

PARALLEL SESSION V

Inorganic Chemistry, Computational Chemistry, and Bioorganic and Medicinal Chemistry

Bis(trifluoromethyl)amines – Synthesis & Properties

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The bis(trifluoromethyl)amino group is a promising building block for pharmaceuticals, agrochemicals, and materials science. The group is available via electrochemical fluorination (ECF) in anhydrous hydrogen fluoride (Simons process) using readily available starting compounds. The synthesis of *N*,*N*-bis(trifluoromethyl)sulfonamides such as $CF_3SO_2N(CF_3)_2$ [1] and $SO_2\{N(CF_3)_2\}_2$ (Fig. 1) [2] via ECF is straightforward and easily scalable. These *N*,*N*-bis(trifluoromethyl)sulfonamides react with metal fluorides or $[N(CH_3)_4]F$ under release of the $\{N(CF_3)_2\}^-$ anion [3]. Salts of the $\{N(CF_3)_2\}^-$ anion [4] and metal complexes [5] (Fig. 1) are valuable starting compounds for the introduction of the bis(trifluoromethyl)amino group into organic molecules. The synthesis of new salts of the $\{N(CF_3)_2\}^-$ anion and their physicochemical properties will be described. The preparation of a variety of different organic molecules that are potential $N(CF_3)_2$-containing building blocks will be presented and the properties of selected molecules will be discussed. In addition, the transformation of bis(trifluoromethyl)amino precursors into mono(trifluoromethyl)amines will be highlighted.

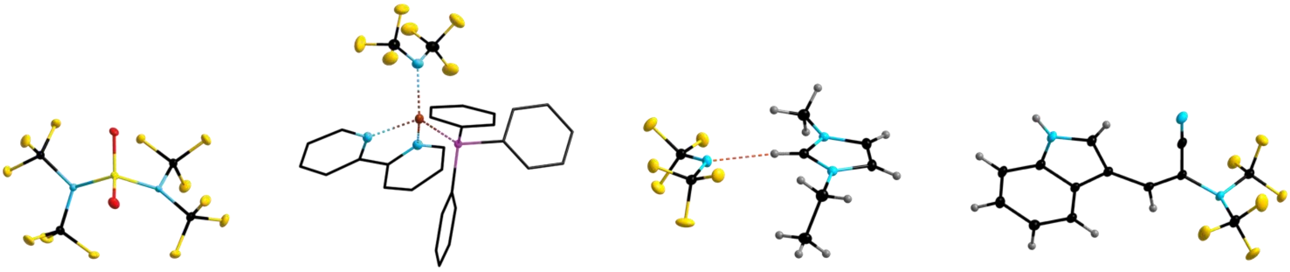

Figure 1. Crystal structures of derivatives of the $\{N(CF_3)_2\}^-$ anion and bis(trifluoromethyl)amines.

References

[1] Sartori, P.; Ignat'ev, N.; Datsenko, S. *J. Fluorine Chem.* **1995**, *75*, 157–161.

[2] Sartori, P.; Ignat'ev, N.; Jüschke, R. *J. Fluorine Chem.* **1997**, *81*, 115–121.

[3] Hilarius, V.; Buchholz, H.; Sartori, P.; Ignatiev, N.; Kucherina, A.; Datsenko, S. Merck Patent GmbH, WO2000046180, 2000.

[4] Breitenstein, C.; Ignat'ev, N.; Frank, W. *J. Fluorine Chem.* **2018**, *210*, 166–177.

[5] Schneider, L. N.; Tanzer Krauel, E.-M.; Deutsch, C.; Urbahns, K.; Bischof, T.; Maibom, K. A. M.; Landmann, J.; Keppner, F.; Kerpen, C.; Hailmann, M.; Zapf, L.; Knuplez, T.; Bertermann, R.; Ignat'ev, N. V.; Finze, M. *Chem. Eur. J.* **2021**, *27*, 10973–10978.

Why Finding the Perfect Sustainable Refrigerant is Harder Than You Think

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Climate change, driven by the continuous increase in anthropogenic greenhouse gas (GHG) emissions, is one of the major environmental concerns of the 21st century. Among these GHGs, hydrofluorocarbons (HFCs) used in refrigeration and cooling systems are being phased out due to their high global warming potential (GWP). However, finding sustainable refrigerants is challenging [1] because they must simultaneously satisfy multiple, often conflicting, criteria, i.e., a good technical performance for the selected application, be safe, environmentally friendly (no ozone depletion potential and ultra-low GWP), and cost-effective. Furthermore, it is highly desirable that the new refrigerants can be used as a drop-in solution in current cooling systems. Unfortunately, as already highlighted by Midgley, improving one factor on the refrigerant molecules (i.e. efficiency) often worsens another (safety or environmental impact). Hence, the search for sustainable refrigerants meeting all requirements continues to be a very active area of research in academia and industry, usually by integrating molecular modeling, experimental testing, and system optimization.

After a general introduction on the challenges and opportunities, this presentation will focus on some of the recent advancements made in this field by a collaborative effort between the teams at the RICH center at Khalifa University and at the Universitat Rovira I Virgili integrating molecular modeling (soft-SAFT, COSMO-RS, and simulations), process modeling, machine learning, and techno-economic assessments to design next-generation refrigerants [2-4]. Focused will be put on the need to provide accurate prediction of the thermodynamic properties, providing insights into the effect of the molecular structure on their macroscopic behaviour, as a first step to design *ad-hoc* fluorinated compounds with the desired properties.

References

[1] McLinden, M.O.; Brown, J.S.; Brignoli, R.; Kazakov, A.F.; Domanski P.A. Nat. Commun., **2017**, 8 1-9.
[2] Albà, C.G.; Alkhatib, I.I.I.; Llovell, F.; Vega, L.F. *Renew. Sustain. Energy Rev.*, **2023**, 188, 113806.
[3] Albà, C.G.; Alkhatib, I.I.I.; Llovell, F.; Vega, L.F. *Appl. Therm. Eng.*, **2024**, 246, 122895.
[4] Alkhatib, I.I.I.; Albà, C.G.; Llovell, F.; Vega, L.F. *Appl. Therm. Eng.,* **2025**, 262, 125316.

Acknowledgments. This work is supported by Khalifa University of Science and Technology under project RIG-2024-041. Resources from the Research and Innovation Center on CO2 and Hydrogen at Khalifa University (project RC2-2019-007) are gratefully acknowledged. Additional financial support has been provided by MICIU/AEI/10.13039/501100011033/ through projects NEW-F-Tech (Ref: TED2021-130959B-I00) and REFCICLA (Ref: PID2023-149713OB-I00), by the European Union NextGenerationEU/PRTR, and by AGAUR as a Consolidated Research Group (SGR 2021-00738).

The Fluorinase – Past, Present and Future

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Adopting enzymatic approaches for the incorporation of fluorine is of significant interest, as such the fluorinase enzyme offers an almost exclusive advantage as it catalyses direct C-F bond formation under aqueous conditions and at ambient temperature.[1] Our interest is in the exploitation of this function utilising the fluorine-18 isotope to permit the direct [^{18}F]radiolabelling of biologically relevant molecules to generate radiotracers for positron emission tomography (PET).[2] Most recently we have looked to explore the substrate tolerance of the fluorinase for heteroalkyl C-2 adenine functionalised substrates[3] in an effort to generate a new class of enzymatically radiolabelled PET tracer targeting the A_{2A} adenosine receptor.

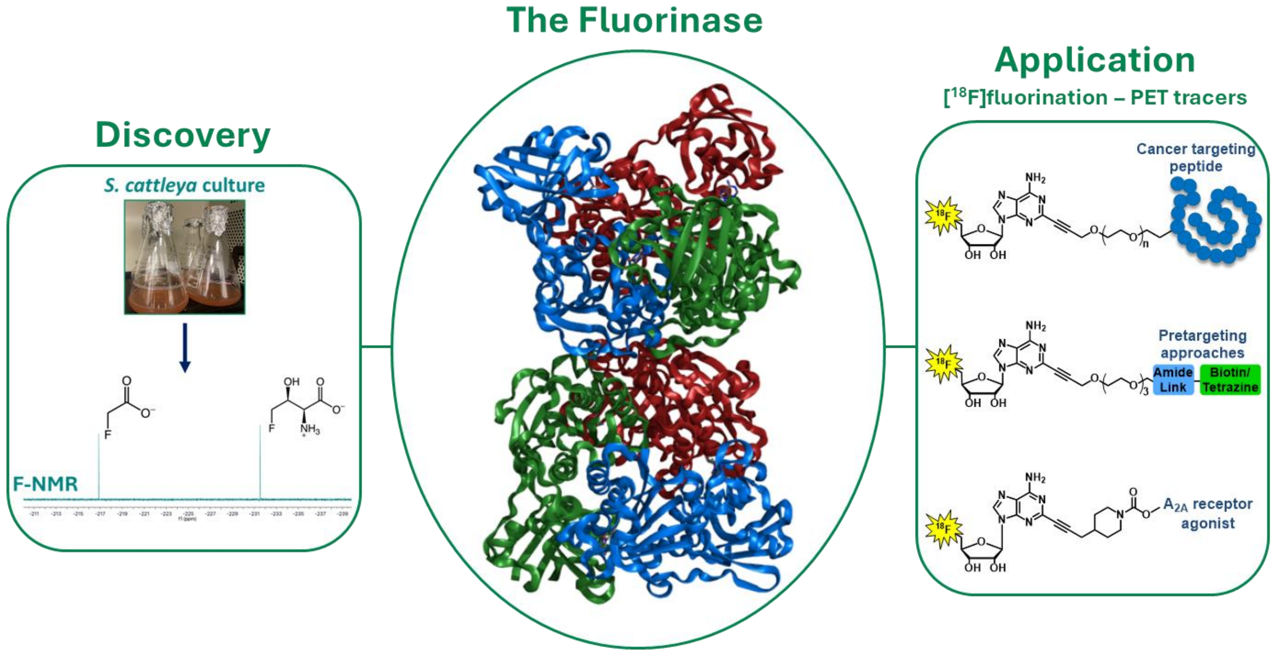

Figure 1. The Fluorinase enzyme – discovery to application for positron emission tomography (PET)

References

[1] O'Hagan, D.; Schaffrath, C.; Cobb, S. L.; Hamilton, J. T. G.; Murphy, C. D. *Nature* **2002**, *416*, 279-279.
[2] Lowe, P. T.; Dall'Angelo, S.; Fleming, I. N.; Piras, M.; Zanda, M.; O'Hagan, D. *Org. Biomol. Chem.* **2019**, *17*, 1480-1486; Thompson, S.; Zhang, Q. Z.; Onega, M.; McMahon, S.; Fleming, I.; Ashworth, S.; Naismith, J. H.; Passchier, J.; O'Hagan, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 8913-8918; Lowe, P. T.; Dall'Angelo, S.; Devine, A.; Zanda, M.; O'Hagan, D. *Chembiochem* **2018**, *19*, 1969-1978; Lowe, P. T.; Dall'Angelo, S.; Mulder-Krieger, T.; Ijzerman, A. P.; Zanda, M.; O'Hagan, D. *Chembiochem* **2017**, *18*, 2156-2164.
[3] Lowe, P. T.; Lueddecke, I.; O'Hagan, D. *Chembiochem* **2025**, *26*. e202400861.

New Avenues in Organoxenon Chemistry

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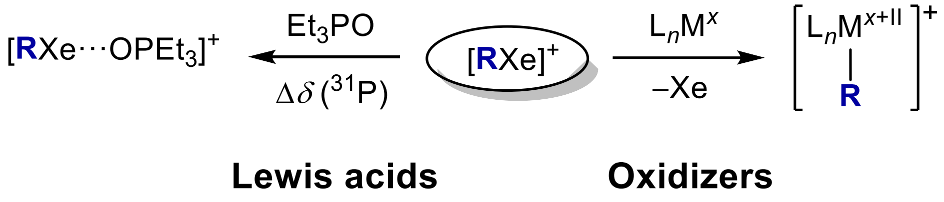
The field of organoxenon chemistry was pioneered by Frohn and Naumann, who independently reported the synthesis of the $[C_6F_5Xe]^+$ cation in 1989.[1] This groundbreaking achievement in the realm of noble-gas chemistry set the basis for the synthesis of many compounds containing Xe−C bonds, including both organoxenonium salts and neutral organoxenon species.[2] Despite the huge number of compounds available, their potential applications in synthesis have remained virtually unexplored. Nevertheless, few examples demonstrating their chemical behavior are known, mainly focused on – but not limited to – salts of the aforementioned $[C_6F_5Xe]^+$ cation or related neutral species containing the C_6F_5 group.[2,3,4]

Here our most recent results in the field of organoxenon chemistry will be presented. We will focus not only on new synthetic approaches towards arylxenon(II) compounds, but also on the description and systematization of their properties and reactivity to unravel their potential as versatile reagents (Scheme 1). Among them, arylxenonium(II) tetrafluoroborates $[RXe][BF_4]$ (R = fluorinated aryl group) are our main target compounds. Our preliminary investigations on their application as electrophilic transfer reagents in organometallic chemistry will be also discussed.



Scheme 1. Reactivity of arylxenonium(II) salts as Lewis acids (left) and oxidizers in organometallic chemistry (right). R = fluorinated aryl group; L_nM = transition metal complex.

References

[1] a) Frohn, H. J.; Jakobs, S. *J. Chem. Soc., Chem. Commun.,* **1989**, 625-627. b) Naumann, D.; Tyrra, W. *J. Chem. Soc., Chem. Commun.,* **1989**, 47-50.
[2] Frohn, H.-J.; Bardin, V. V. *Organometallics,* **2001**, *20 (23)*, 4750-4762.
[3] Frohn, H.-J.; Bardin, V. V. *Inorg. Chem.,* **2012**, *51 (4)*, 2616-2620.
[4] Frohn, H.-J.; Theißen, M. *J. Fluorine Chem.,* **2004**, *125 (6)*, 981-988.

Pentafluorophosphates as Biomimetics of Phosphopeptides and Phosphoproteins

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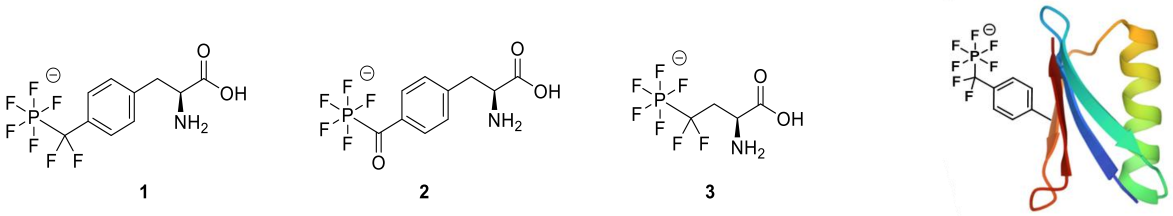
Many biological processes are regulated by protein kinases or phosphatases, which influence cellular signal transduction by adding or cleaving off phosphate groups from their targets. Our group has introduced a novel, non-cleavable phosphate biomimetic that carries only one negative charge and demonstrates enhanced lipophilicity compared to other phosphonate analogues.[1] The pentafluorophosphato difluoromethyl group was implemented for the novel amino acids PF_5-tyrosine **1** and -serine **3**. The difluoromethyl group in **1** was hydrolyzed with aqueous HF to yield the acyl PF_5-tyrosine **2**.

PF_5-tyrosine structures **1** and **2** were identified as potent binders of the protein tyrosine phosphatase PTP1B with more than 25-fold improved affinity compared to the gold standard biomimetic, phosphonodifluoromethyl-phenylalanine.[1] N- and C-terminal elongations yielded inhibitors in the low µM range, which are currently tested in cellular assays.



1 2 3

Figure 1. PF_5-amino acids PF_5-Tyr **1**, **2**, PF_5-Ser **3**, and PF_5-Tyr-GB1.

Amino acid **1** was incorporated into three different proteins by genetic encoding using an orthogonal translation system. The protein GB1 carrying the PF_5-tyrosine amino acid exhibited strong inhibition of the phosphatases PTP1B and SHP2, whereas native GB1 showed no binding. The PF_5 residue was also hydrolyzed to the CF_2-phosphonate biomimetic. This method could be generally used for the facile production of phosphoprotein mimetics.

The synthesis of PF_5-serine was established starting from commercially available Boc-L-serine. Properties of the new amino acid and oligomers of it are currently investigated, yielding first interesting results in the area of antimicrobial peptides.

References

[1] M. Accorsi, M. Tiemann, L. Wehrhan, L.M. Finn, R. Cruz, M. Rautenberg, F. Emmerling, J. Heberle, B.G. Keller, J. Rademann. *Angew. Chem. Int. Edit*. **2022**, *61,* e202203579.

Synthesis and Reactivity of Fluorinated Alkyl Halonium Ions

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The only two literature-known synthetic methods to access alkyl chloronium ions are either the protonation of chloroalkanes by Brønsted superacids[1] or the halide abstraction by Lewis superacids.[2] However, these methods are not applicable for the synthesis of fluorinated alkyl chloronium ions, due to the low proton affinity and the high stability of fluorinated chloroalkanes.

We developed a synthetic route towards fluorinated alkyl chloronium ions by utilizing the strong oxidizing xenonium ion $[XeOTeF_5]^+$, that converts the starting material CH_2ClCF_3 into $[Cl(CH_2CF_3)_2]^+$ by oxidation of the chlorine atom.[3] The chloronium ion is a strong hydride abstractor and activates alkanes such as *n*-butane, *n*-pentane or cyclohexane, yielding branched carbocations. In addition, the chloronium salt is used as powerful electrophilic transfer reagent of the CH_2CF_3 group, enabling the trifluoroethylation of weak nucleophiles such as perfluoropyridine and the synthesis of fluorinated alkyl bromonium and iodonium ions (Figure 1).

The properties of the cations $[Cl(CH_2CF_3)_2]^+$, $[Br(CH_2CF_3)_2]^+$ and $[I(CH_2CF_3)_2]^+$ and attempts towards other fluorinated alkyl halonium ions will be discussed.

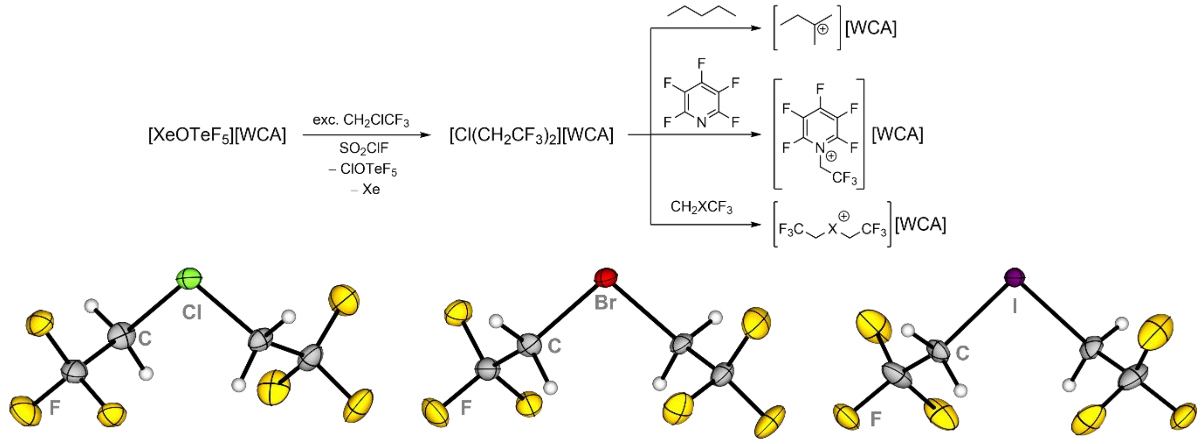

Figure 1. Synthesis and reactivity of the chloronium salt $[Cl(CH_2CF_3)_2][Sb(OTeF_5)_6]$ and the molecular structure of the halonium cations $[Cl(CH_2CF_3)_2]^+$ (left), $[Br(CH_2CF_3)_2]^+$ (middle) and $[I(CH_2CF_3)_2]^+$ (right) in the solid state. The anion $[Sb(OTeF_5)_6]^-$ is omitted for clarity.

References

[1] a) Hämmerling, S.; Thiele, G.; Steinhauer, S.; Beckers, H.; Müller, C.; Riedel, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 9807 b) Stoyanov, E. S.; Stoyanova, I. V.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2010**, *132*, 4062.
[2] Olah, G. A.; Melby, E. G. *J. Am. Chem. Soc.* **1972**, *94*, 6220.
[3] Fischer, L.; Lee, M. H.; Kim, I.; Wiesner, A.; Hoffmann, K. F.; Hasenstab-Riedel, S. *Angew. Chem. Int. Ed.* **2024**, e202407497.

Phosphonate Analogues of Fluorophenylglycines as Potential Inhibitors of Human Urokinase Plasminogen Activator: Synthesis, Structure and Anticancer Activity

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Phosphonate analogues of α-amino acids are increasingly valued for their significant potential in medicinal chemistry. Fluorine is an element that plays a huge role in modulating the properties of organic compounds. These two pharmacophores were combined in the synthesis of new α-aminophosphonates obtained by diastereoselective hydrophosphonylation of imines prepared by an environmentally friendly mechanochemical approach.

SwissADME analysis suggested favourable drug-like properties of the α-aminophosphonates and indicated their potential for interaction with diverse biological targets including proteases. Screening against ten cancer cell lines from seven types of cancer showed that most of the compounds tested exhibited superior activity and selectivity over 5-fluoro-2'-deoxyuridine used as a standard anticancer drug. Molecular docking highlighted the strong binding of one of the α-aminophosphonates to the urokinase-type plasminogen activator (uPA) protein, suggesting the anti-metastatic potential of the compound. These findings enable to position the newly synthesized α-aminophosphonates as promising scaffolds for developing targeted anticancer therapies for metastatic cancers characterized by elevated uPA expression.

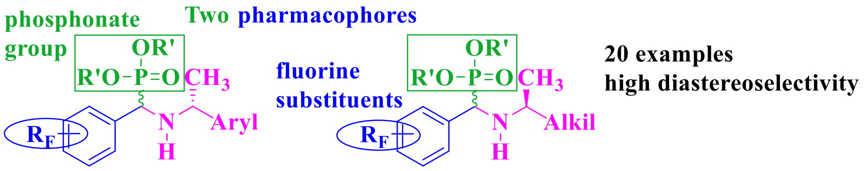

Figure 1. General structure of the α-aminophosphonates designed.

References

[1] K. Ciesielska, D. Wawrzyniak, G. Dutkiewicz, M. Kubicki, W. Jankowski, M. Hoffmann, K. Kamel, K. Rolle, D. Pluskota-Karwatka. *Europ. J. Med. Chem.,* **2025**, *283*, 117116.
[2] K. Ciesielska, M. Hoffmann, M. Kubicki, D. Pluskota-Karwatka. *Molecules,* **2022**, *27*, 4557.
[3] A. Daina, O. Michielin, V. Zoete, *Sci. Rep*. **2017**, *7,* 42717.
[4] A. Mucha, P. Kafarski, Ł. Berlicki. *J. Med. Chem.,* **2011**, *54*, 5955.
[5] E.P. Gillis, K.J. Eastman, M.D. Hill, D.J. Donnelly, N.A. Meanwell, *J. Med. Chem.,* **2015**, *58*, 8315.
[6] K. Dass, A. Ahmad, A.S. Azmi, S.H. Sarkar, F.H. Sarkar, *Cancer Treat. Rev*., **2008**, *34*,122.

Fluorination of Rotaxanes for Sensitive ^{19}F MR-Fluorescence dual Imaging

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Motion state significantly influences the sensitivity and responsiveness of imaging agents, presenting a formidable challenge to effectively exploit. To this ende, we utilized [5]rotaxane to precisely control the motions of fluorines and tetraphenyl ethylene (TPE) simultaneously, yielding a sensitive and stimulus-responsive dual imaging agent for fluorine-19 mag-netic resonance imaging (^{19}F MRI) and fluorescence imaging (FLI) with an unprecedented micromolar sensitivity. The [5]rotaxane seamlessly integrates 144 chemically equivalent fluorines to produce an intense singlet ^{19}F peak for sensitive ^{19}F MRI, while enabling stimulus responsiveness and increasing signal intensity (SI) by an additional 45% through precisely controlling intramolecular wheel motions. Extensive spectroscopic and imaging studies, along with molecular dynamics sim-ulations, highlight [5]rotaxane formation, wheel "stationing-shuttling", and the introduction of fluorous bulky perfluoro-*tert*-butoxymethyl (PFBM) groups as robust motion control strategies. This research also provides valuable insights into the structure, dynamics, aggregation behavior, and potential applications of [5]rotaxanes as dual imaging agents.

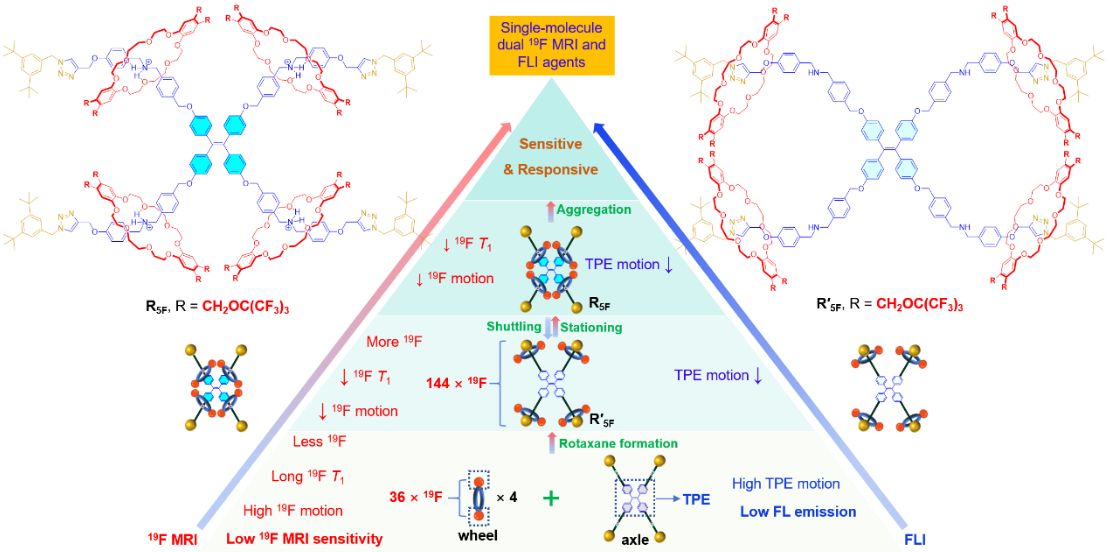

Figure 1. Mechanical interlocking of 144 symmetrical ^{19}F and TPE for sensitive ^{19}F MR-FL dual imaging.

References

[1] Yang, L.; Wang, F.; Li, Y.; Zhou, R.; Li, A.; Wu, T.; Qiu, M.; Zhang, L.; Yang, M.; Zhou, X.; Jiang, Z.-X.; Chen, S. *J. Am. Chem. Soc.* **2025**, doi.org/10.1021/jacs.5c00429

[2] Yang, L.; Li, Y.; Jiang, M.; Zhou, R.; Cong, H.; Yang, M.; Zhang, L.; Li, S.; Yang, Y.; Liu, M.; Zhou, X.; Jiang, Z.-X.; Chen, S. *Chin. Chem. Lett.* **2024**, *35*, 109512.

[3] Li, Y.; Luo, M.; Jiang, M.; Zhou, R.; Yang, W.; Li, S.; Wang, F.; Zhu, L.; He, P.; Yang, M.; Zhou, X.; Jiang, Z.-X.; Chen, S. *Anal. Chim. Acta.* **2024**, *1319*, 342983.

[4] Wu, T.; Li, A.; Chen, K.; Peng, X.; Zhang, J.; Jiang, M.; Chen, S.; Zheng, X.; Zhou, X.; Jiang, Z.-X. *Chem. Comm.* **2021**, *57*, 7743-7757.

Phosphonium SF_5^- Salts Derived from SF_6 as Oxidative Fluorination and Deoxyfluorination Agents

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Fluorinated organic and inorganic compounds play a crucial role in pharmaceuticals, agriculture, and materials. However, their synthesis often relies on hazardous and highly reactive reagents that are challenging to handle. Sulfur hexafluoride (SF_6) has recently gained attention as a nontoxic fluorine source for such transformations.[1] SF_6 is widely used in industry and produced on a large scale, but its extreme greenhouse gas potential necessitates strict regulations against its atmospheric release. Converting end-of-life SF_6 into value-added compounds offers a promising alternative to its destruction.

Our group has demonstrated that electron-rich phosphines activate SF_6 via nucleophilic attack, forming crystalline $[FPR_3]^+[SF_5]^-$ salts.[2,3] Herein, we present applications of these thermally stable salts in fluorination reactions. Organic molecules with functional groups such as alcohols, anhydrides, and amides undergo deoxyfluorinations, while main-group elements and transition metal carbonyls undergo oxidative fluorinations, giving access to novel fluorinated anions.

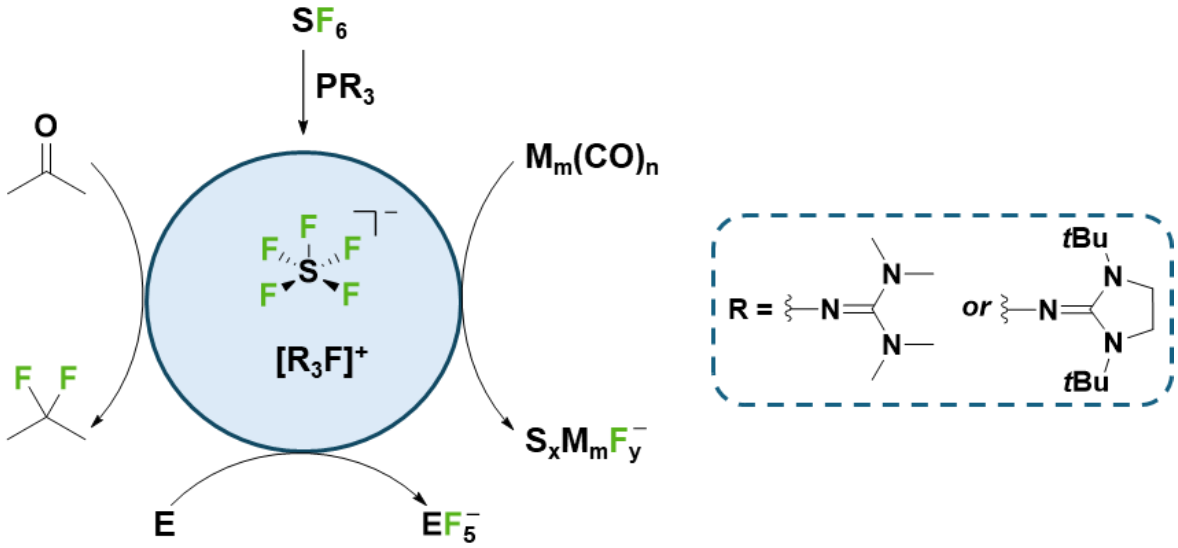

Figure 1. Generation of SF_5^- salts from SF_6 and their application in fluorinations.

References

[1] Rombach, D.; Wagenknecht, H.-A. *Synthesis* **2022**, 54, 4883–4894.

[2] Eder, T.; Buß, F.; Wilm, L. F. B.; Seidl, M.; Podewitz, M.; Dielmann, F. *Angew. Chem. Int. Ed.* **2022**, e202209067.

[3] Röthel, M. B.; Schöler, A.; Buß, F.; Löwe, P.; Dielmann, F. *Chem. Eur. J.* **2024**, 30, e20240202.

Scientific Programme: Talks

Thursday, August 7th, 2025

Thursday, August 7th, 2025

PLENARY SESSION - FENG-LING QING

Room: Auditorium II
Chair: Matthew Hopkinson, Newcastle University, UK

09:00 – 10:00	**SYNTHESIS AND APPLICATION OF PENTAFLUOROSULFANYL (SF_5)-CONTAINING REAGENTS**
PL	**Feng-Ling Qing**, Shanghai Institute of Organic Chemistry, China

KEYNOTE SESSION - BERTHOLD HOGE

Room: Auditorium II
Chair: Joseph Thrasher, Clemson University, USA

10:00 – 10:45	**PERFLUOROORGANYL GALLIUM AND INDIUM CHEMISTRY: THE FIRST MAIN GROUP ELEMENT LEWIS ACID THIONYL CHLORIDE ADDUCT AND ITS CHEMISTRY**
KN	**Berthold Hoge**, Bielefeld University, Germany

PARALLEL SESSION VI – ORGANIC & ORGANOMETALLIC CHEMISTRY

Room: Auditorium II
Chair: David Vicic, Lehigh University, USA

11:15 – 11:35	**RHODIUM-MEDIATED C-H AND C-F BOND ACTIVATION TO ACCESS FLUORINATED ALKENE DERIVATIVES**
IL	**Thomas Braun**, Humboldt University Berlin, Germany
11:35 – 11:55	**MECHANISTIC INSIGHT ON COPPER-MEDIATED TRIFLUOROMETHYLATION**
IL	**Qilong Shen**, Shanghai Institute of Organic Chemistry, China
11:55 – 12:15	**ORGANOFLUORINE TRANSITION METAL CHEMISTRY MEETS CARBENE CHEMISTRY**
IL	**Miguel Baya**, Universidad de Zaragoza, Spain
12:15 – 12:30	**ORGANOMETALLIC CHEMISTRY OF THE PERFLUORINATED CP* LIGAND $[C_5(CF_3)_5]^-$**
Oral	**Moritz Malischewski**, Freie Universität Berlin, Germany
12:30 – 12:45	**MIGRATORY ALLYLIC C–F BOND FUNCTIONALIZATION**
Oral	**Jean-Denys Hamel**, University of Lethbridge, Canada
12:45 – 13:00	**SYNTHETIC APPROACH TO CF_3-ALKENYL DERIVATIVES OF AMINO ACIDS**
Oral	**Katarzyna Koroniak-Szejn**, Adam Mickiewicz University, Poland

PARALLEL SESSION VI – CONTAMINANTS OF EMERGING CONCERN & MATERIALS & ORGANIC CHEMISTRY

Room: 3A
Chair: Cormac Murphy, University College Dublin, Ireland

11:15 – 11:35 IL	**SUPRAMOLECULAR ARCHITECTURES AND HYDROGELS BASED ON FLUORINATED AMINO ACIDS** **Valentina Dichiarante**, Politecnico di Milano, Italy
11:35 – 11:50 Oral	**COMPLETE MINERALIZATION OF LITHIUM BIS(PENTAFLUOROETHANE-SULFONYL)IMIDE AND RELATED ELECTROLYTE FLUOROCHEMICALS USING SUPERHEATED WATER** **Hisao Hori**, Kanagawa University, Japan
11:50 – 12:05 Oral	**OCCURRENCE, DISTRIBUTION AND FATE OF FLUORINE DURING PHOSPHATE ORE PROCESSING** **Kamal Benali**, Fluoralpha, Morocco
12:05 – 12:20 Oral	**ORGANOCATALYZED SYNTHESIS AND DEPOLYMERIZATION OF FLUORINATED POLYSILOXANES, A ROUTE TO THEIR CHEMICAL RECYCLING** **Vincent Ladmiral**, National Centre for Scientific Research (CNRS), France
12:20 – 12:35 Oral	**INNOVATIVE BIFUNCTIONAL SILOXANE AND THEIR POTENTIAL APPLICATION** **Joanna Karasiewicz**, Adam Mickiewicz University Poznan, Poland
12:35 – 12:50 Oral	**IMPACTING HIGH PRESSURE STRUCTURAL TRANSITION OF ALKALI METAL HEXAFLUORIDES** **Kevin Lemoine**, Université Clermont Auvergne, France
12:50 – 13:05 Oral	**SYNTHESIS OF α-FLUOROALKYLATED PYRIDINES AND PYRIMIDINES VIA DIRECT FLUORINATION WITH NFSI** **Petro Onys’ko**, National Academy of Sciences of Ukraine, Ukraine
13:05 – 13:20 Oral	**AMINE-FUNCTIONALIZED FLUOROARENES FOR ENERGY AND ENVIRONMENTAL APPLICATIONS** **Anastasios Stergiou**, Politecnico di Milano, Italy
13:20 – 13:35 Oral	**MANAGED AQUIFER RECHARGE: A NEW FRONTIER FOR ADDRESSING EMERGING CONTAMINANTS** **Srdana Kolakovic**, NOVA University Lisbon, Portugal

PARALLEL SESSION VI – ORGANIC CHEMISTRY

Room: 3B
Chair: Gavin Chit Tsui, The Chinese University of Hong Kong, China

11:15 – 11:35 IL	**CHEMICAL RECYCLING OF FLUOROCARBONS BY TRANSFER FLUORINATION** **Mark R. Crimmin**, Imperial College London, UK
11:35 – 11:55 IL	**THE ROLE OF ELECTROSTATIC NON-CONVENTIONAL HYDROGEN BONDING INTERACTIONS IN ORGANOFLUORINE COMPOUNDS** **Rodrigo A. Cormanich**, Universidade Estadual de Campinas, Brazil

11:55 – 12:15	**RECENT ADVANCES IN THE SYNTHESIS OF PENTAFLUOROSULFANYLATED MOLECULES**
IL	**Jean-François Paquin**, Université Laval, Canada
12:15 – 12:35	**EXPERIMENTAL AND THEORETICAL STUDY OF DIFLUOROBENZIMIDAZOLES**
IL	**Jaroslav Kvíčala**, University of Chemistry and Technology, Czechia
12:35 – 12:50	**SHELF-STABLE REAGENT FOR RADICAL PENTAFLUOROSULFANYLATION**
Oral	**Yi Yang**, Université Claude Bernard Lyon1, France
12:50 – 13:05	**TETRAFLUOROPYRIDYL GROUPS; APPLICATIONS IN MOLECULAR FUNCTIONALISATION**
Oral	**William D. G. Brittain**, Durham University, UK
13:05 – 13:20	**THIONYL FLUORIDE AS A SULFUR(IV) S_UFE_X HUB FOR THE EFFICIENT SYNTHESIS OF SULFINAMIDES AND SULFINATE ESTERS**
Oral	**William P. Chappell**, The University of British Columbia, Canada

PARALLEL SESSION VII – INORGANIC CHEMISTRY

Room: Auditorium II
Chair: Miroslav Boča, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia

14:30 – 14:50	**EXPLORING XENON DIFLUORIDE COORDINATION COMPOUNDS: FROM INITIAL DISCOVERIES TO NOVEL SO_3F^- ANION**
IL	**Gašper Tavčar**, Jožef Stefan Institute, Slovenia
14:50 – 15:10	**MANIPULATING F···F INTERACTIONS FOR METAL EXTRACTIONS**
IL	**Robert J. Baker**, University of Dublin, Trinity College, Ireland
15:10 – 15:25	**FLUORINATION BY SOLID-GAS REACTION OF HIGH-PERFORMANCE COMPOUNDS FOR RECHARGEABLE BATTERIES**
Oral	**Saida Moumen**, Clermont-Auvergne University, France
15:25 – 15:40	**SIMPLE ACCESS TO A SERIES OF HIGHER SUBSTITUTED PENTAFLUOROORTHOTELLURATE-BASED SILANES AND GERMANES**
Oral	**Friederike Oesten**, Freie Universität Berlin, Germany
15:40 – 15:55	**SYNTHESIS AND REACTIVITY OF ZINC-FLUORIDE COORDINATION COMPLEXES**
Oral	**Aaranjah Vickneswaran**, Imperial College London, UK
15:55 – 16:10	**THE TRIFLUOROOXYGENATE ANION $[OF_3]^-$: SPECTROSCOPIC EVIDENCE FOR A BINARY, HYPERVALENT OXYGEN SPECIES**
Oral	**Deniz F. Meyer**, Freie Universität Berlin, Germany
16:10 – 16:25	**ELECTROCHEMICAL FLUORINATION – A VERSATILE TOOL FOR THE LARGE SCALE SYNTHESIS OF PARTIALLY FLUORINATED BUILDING BLOCKS**
Oral	**Tanja Knuplez**, University of Würzburg, Germany
16:25 – 16:40	**NITROSYL FLUORIDE (FNO) AND NITRYL FLUORIDE (FNO_2) AS FLUORINATING AGENTS FOR INORGANIC MATERIALS**
Oral	**Batiste Clavier**, Université Clermont Auvergne, France

PARALLEL SESSION VII – ORGANIC CHEMISTRY

Room: 3A
Chair: Frédéric Leroux, University of Strasbourg - CNRS, France

14:30 – 14:50	**AMINOPHOSPHONATES BEARING FLUORINE ATOMS AS INHIBITORS OF AMINOPEPTIDASES – SYNTHESIS AND PROPERTIES**
IL	**Henryk Koroniak**, Adam Mickiewicz University, Poznań, Poland
14:50 – 15:10	**NOVEL APPROACHES IN ASYMMETRIC CATALYTIC SYNTHESIS OF HALO-ORGANIC COMPOUNDS**
IL	**Mark Gandelman**, Technion - Israel Institute of Technology, Israel
15:10 – 15:30	**THE VALUE OF FLUORINE IN AGRICULTURAL CHEMISTRY**
IL	**Michael Rack**, BASF SE, Germany
15:30 – 15:45	**EFFECT OF AMINE DEPROTONATION ON S_UFE_X: SYNTHESIS OF SULFONAMIDES**
Oral	**Jan Dudziński**, University of Warsaw, Poland
15:45 – 16:00	**AN UNUSUAL REACTION OF FLUORINE SUBSTITUTION IN PENTAFLUOROIODO- AND PENTAFLUOROBROMOBENZENES BY AMINO SPECIES RUNNING AT AMBIENT CONDITIONS**
Oral	**Evgeny Goreshnik**, Jožef Stefan Institute, Slovenia
16:00 – 16:15	**CROSS-COUPLING REACTIONS USING MULTIHALOGENATED ALKENES SYNTHESIZED FROM HALOTHANE**
Oral	**Yukiko Karuo**, Setsunan University, Japan
16:15 – 16:30	**DEFLUORINATIVE SYNTHESIS OF MONOFLUOROALKENES VIA PHOTOREDOX C–C COUPLING OF α-AMINOALKYL RADICALS AND ALLYLIC DIFLUORIDES**
Oral	**Taylor Semeniuk**, University of Lethbridge, Canada

PARALLEL SESSION VII – ORGANIC CHEMISTRY

Room: 3B
Chair: Frederik Diness, Roskilde University, Denmark

14:30 – 14:50	**PERFLUORO-TERT-BUTY ANION: PREPARATION, STRUCTURE, AND REACTIVITY**
IL	**Jinbo Hu**, Chinese Academy of Sciences, China
14:50 – 15:10	**ON THE IMPORTANCE OF MICHAELIS–MENTEN KINETICS**
IL	**Rimantas Knizikevičius**, Kaunas University of Technology, Lithuania
15:10 – 15:30	**FROM TRIFLUOROMETHOXYLATION TO DIFLUOROPHOSGENE CHEMISTRY: A JOURNEY WITH 2,4-DINITRO-TRIFLUOROMETHOXYBENZENE (DNTFB)**
IL	**Thierry Billard**, University of Lyon, France
15:30 – 15:45	**LEWIS ACID-CATALYZED CARBOFLUORINATION VIA FLUORIDE RECYCLING**
Oral	**Christine M. Le**, York University, Canada
15:45 – 16:00	**REACTIONS OF HEXAFLUOROTHIOACETONE DIMER (HFTAD) WITH TERPENES**
Oral	**Viacheslav Petrov**, Fluorinova LLC, USA

16:00 – 16:15	**HF SHUTTLING FOR THE CHEMICAL RECYCLING OF FLUOROCARBONS**
Oral	**Shannon E. S. Farley**, Imperial College London, UK

FLASH PRESENTATIONS

Room: Auditorium II
Chair: Maik Finze, University of Wurzburg, Germany

17:00 – 17:05	**ACTIVATION OF PERFLUORO(METHYL VINYL ETHER) AT Rh(I) PHOSPHINE COMPLEXES: METAL-CENTERED VERSUS PHOSPHINE MEDIATED DECARBONYLATION**
FP	**Soodeh Mollasalehi**, Humbold-Universität zu Berlin, Germany
17:05 – 17:10	**C–F BOND ACTIVATION OF FLUOROALKANES VIA GERMYLIUM IONS CATALYSIS**
FP	**Julie Borel**, Humbold-Universität zu Berlin, Germany
17:10 – 17:15	**RESPIROMETRIC ANALYSIS FOR MONITORING THE MICROBIAL ACTIVITY DURING EXPOSURE TO PERFLUOROBUTANESULFONIC AND PERFLUOROHEXANESULFONIC ACID**
FP	**Natalija Petronijevic**, University of Belgrade, Serbia
17:15 – 17:20	**NOVEL HEXAFLUOROSULFUR ACTIVATION UTILIZING AN ORGANIC PHOTOREDOX CATALYST**
FP	**Max Flügge**, Karlsruhe Institute of Technology, Germany
17:20 – 17:25	**INVESTIGATING THE SITE-SPECIFIC IMPACT OF FLUORINE SUBSTITUTION ON AROMATIC INTERACTIONS IN A TRYPTOPHAN ZIPPER PEPTIDE**
FP	**David Reiter**, Freie Universität Berlin, Germany
17:25 – 17:30	**DEVELOPMENT AND CHARACTERIZATION OF INNOVATIVE MATERIALS FOR PHOTOCATALYTIC DEGRADATION OF PERFLUOROOCTANOIC ACID**
FP	**Kristina Kasalica**, University of Belgrade, Serbia
17:30 – 17:35	**SEARCH FOR NOVEL SUPERCONDUCTORS IN A CHEMICAL CAPACITOR SETUP**
FP	**Dawid Ciszewski**, University of Warsaw, Poland
17:35 – 17:40	**APPLICATION OF CF_3-NITRILE IMINES IN THE SYNTHESIS OF UNSYMMETRICAL N',N'-TRIFLUOROACETOHYDRAZIDES**
FP	**Adrian Warcholiński**, University of Lodz, Poland
17:40 – 17:45	**DESULFURATIVE FLUORINATION OF ALKYL PHENYL SULFIDES**
FP	**Brian Durkan**, Royal College of Surgeons, Ireland
17:45 – 17:50	**EXPANDING THE CHEMICAL SPACE OF PENTAFLUOROSULFANYL-CONTAINING COMPOUNDS**
FP	**Lujie Xu**, University of Zurich, Switzerland
17:50 – 17:55	**SEMI-CATALYTIC TRIFLUOROMETHYLATION USING TETRAKIS(TRIFLUOROMETHYLCOPPER)**
FP	**Petr Pospíšil**, Czech Academy of Sciences, Czechia
17:55 – 18:00	**INVESTIGATION OF DICATIONIC IONIC LIQUIDS WITH DIFLUOROPHOSPHATE ANION**
FP	**Kentaro Kamada**, Kyoto University, Japan

18:00 – 18:05	**FROM TRIFLUOROMETHYL TO PENTAFLUOROETHYL: NEW APPROACHES IN GOLD(III) COMPLEXES STABILIZATION**
FP	**Alba de Toro**, Universidad de Zaragoza CSIC, Spain
18:05 – 18:10	**THE BIOINORGANIC IMPACT OF FLUORINE STUDIED BY VIBRATIONAL SPECTROSCOPY**
FP	**Soumyamoy Pathak**, Freie University Berlin, Germany
18:10 – 18:15	**FUNCTIONALIZATION OF NANODIAMONDS WITH PERFLUOROPOLYETHER PEROXIDE VIA A FACILE THERMOCHEMICAL PROCESS**
FP	**Davide Ceriotti**, Politecnico di Milano, Italy

PARALLEL SESSION VI

Organic and Organometallic Chemistry

Rhodium-Mediated C-H and C-F Bond Activation to Access Fluorinated Alkene Derivatives

Thomas Braun,[1,*] Maria Talavera,[1] Cortney von Hahmann,[1] Soodeh Mollasalehi,[1] Mike Ahrens[1]

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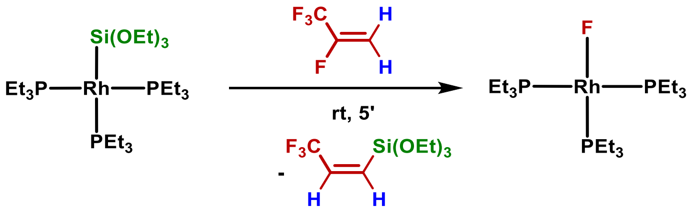
Useful methods for a metal-mediated derivatization of fluorinated molecules are often based on C−H or C−F bond activation reactions.[1] In order to make C−F bond cleavage steps feasible, other strong element−fluorine bonds such as H−F or Si−F bonds have to be formed. Thus, at rhodium, highly reactive Rh(I) species such as [Rh(H)(PEt_3)$_3$], [Rh{Si(OEt)$_3$}(PEt_3)$_3$] or [Rh($GePh_3$)(PEt_3)$_3$] can serve as suitable tools to induce a C−F bond activation step, but also C−H bond activation reactions.[2] Stoichiometric studies at the rhodium complexes as well as initial catalytic reactions for the hydrodefluorination, silylation or germylation of olefinic precursors will be described (Scheme). In another spin-off catalytic cross-coupling reactions were developed, which are characterized by an outer-sphere C-C coupling step.



Scheme 1. A Rh silyl complex for the silylation of a fluorinated olefin.

References

[1] Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun T. *Chem. Rev.* **2015**, *115*, 931-972; M. Talavera, T. Braun, *Synlett* **2020**, *31*, 1760-1774.

[2] Talavera, M.; Braun T. *Chem. Sci.* **2022**, *13*, 1130-1135; Talavera, M.; Müller, R.; Ahrens, T.; von Hahmann, C. N.; Braun-Cula, B.; Kaupp, M.; Braun, T. *Faraday Discuss.* **2019**, *220*, 328-349; Talavera, M.; von Hahmann, C. N. ;Müller, R.; Ahrens, M. ; Kaupp, M.; Braun, T. *Angew. Chem. Int. Ed.* **2019**, *58*, 10688-10692; Talavera, M.; Mollasalehi, S.; Braun, T. *Chem. Sci.* **2024**, *15*, 8472–8477.

Mechanistic Insight on Copper-Mediated trifluoromethylation

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Copper-mediated trifluoromethylation represents one of the most efficient methods that may have potentially applications in pharmaceutical and agrochemical industry. Mechanistically, it was proposed that the reaction proceeds via a Cu(I)/Cu(III) catalytic cycle. Nevertheless, both the Cu(I) species [$Cu^{I}CF_3$] and the putative key product-forming Cu(III) intermediate [$Ar\text{-}Cu^{III}\text{-}CF_3$] remain elusive. We now report the synthesis, characterization of both intermediates including stable Cu(I) species [$n$$Bu_4N$]$^+$[$Cu^{I}(CF_3)_2$]$^-$ as well as Cu(III) complexes including [$n$$Bu_4N$]$^+$[$Cu^{III}(Ar)(CF_3)_3$]$^-$ and [(bpy)$Cu^{III}(CF_3)_2(Ar)$]. Mechanistic investigations on oxidative addition of alkyl halides to Cu(I) species and reductive elimination from Cu(III) complexes were discussed in detail.

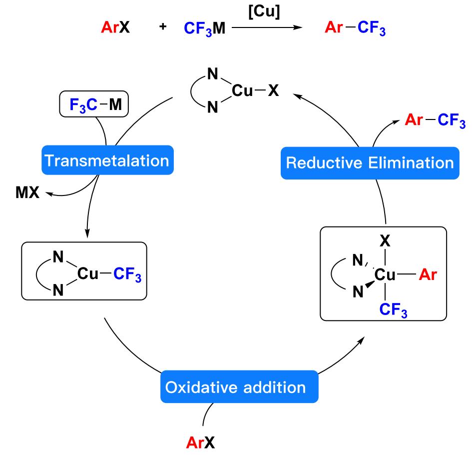

Figure 1. Catalytic cycle for copper-catalyzed trifluoromethylation of aryl halides

References

[1] Luo, Y.-R.; Li, Y.-L.; Wu, J.; Xue, X.-S.; Hartwig, J. F.; Shen, Q. *Science*, **2023**, *381*, 1072–1079.
[2] Lu, Z.-H.; Liu, H.; Liu, S.-Y.; Leng, X.-B.; Lan, Y.; Shen, Q. *Angew. Chem. Int. Ed.* **2019**, *58*, 8510–8514.
[3] Liu, S.-S.; Liu, H.; Liu, S.-H.; Lu, Z.-H.; Lu, C.-H.; Leng, X.-B.; Lan, Y.; Shen, Q. *J. Am. Chem. Soc.* **2020**, *142*, 9785–9791.
[4] Liu, H.; Wu, J.; Jin, Y.-X.; Leng, X.-B.; Shen, Q. *J. Am. Chem. Soc.* **2021**, *143*, 14367-14378.
[5] Wang, G.-Y.; Li, M.; Leng, X.-B.; Xue, X.-S.; Shen, Q. *Chin. J. Chem.* **2022**, *40*, 1924-1930.
[6] Weng, Y.-C.; Jin, Y.-X.; Wu, J.; Leng, X.-B.; Lou, X.-B.; Geng, F. S.; Hu, B.-W.; Wu, B.-T.; Shen Q. *J. Am. Chem. Soc.* **2024**, *146*, 23555-22565.
[7] Wang, G.-Y.; Li, H.-Y.; Leng, X.-B.; Lu, L.; Shen, Q. *Chin. J. Chem.* **2024**, *42*, 1107−1113
[8] Weng, Y.-C.;Pan, D.; Wu. J.; Leng, X.-b.; xue, X.-S.; Shen, Q. *Chem. Eur. J.* **2025**, e202403620

Organofluorine Transition Metal Chemistry meets Carbene Chemistry

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Trifluoromethyl transition metal (TM) chemistry is emerging as a fast-moving and exciting research field. We recently developed a convenient synthesis of the homoleptic $[Pd(CF_3)_4]^{2-}$ (**1**) complex.[1] In contrast to its isoelectronic Ag(III) counterpart, $[Ag(CF_3)_4]^-$,[2] this d^8 square-planar palladium species exhibits an electronic structure consistent with a regular ligand field.

Interestingly, a fluoride ion can be readily abstracted from **1** yielding the highly electrophilic difluorocarbene $[Pd(CF_2)(CF_3)_3]^-$ (**2**) complex. This transient species, detected in solution (figure 1), enables the preparation of a range of Fisher-type F, N- and N, N- stabilized carbene complexes, with formulae $[Pd\{CF(NR_2)\}(CF_3)_3]^-$ and $[Pd(NHC)(CF_3)_3]^-$. Building on these investigations, we have developed a novel synthetic procedure that allows the preparation of a broad series of Fisher-type carbene palladium complexes stabilized by various heteroatoms.

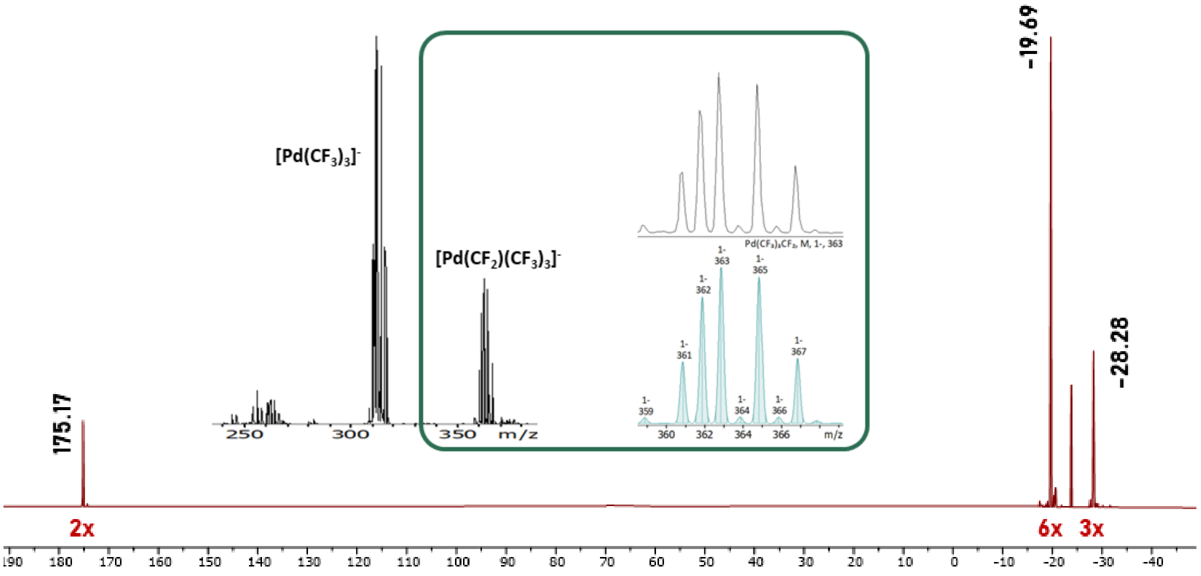

Figure 1. Spectroscopic detection of the difluorocarbene complex $[Pd(CF_2)(CF_3)_3]^-$: ^{19}F NMR (-60 °C, CD_2Cl_2) and ESI-MS (including simulation).

References

[1] Joven-Sancho, D., Baya, M.; Martín, A.; Orduna, J.; Menjón, B. *Angew. Chem. Int. Ed.* **2024**, *63*, e202403108.

[2] Joven-Sancho, D.; Baya, M.; Martín, A.; Menjón, B. *Chem. Eur. J.* **2018**, *24*, 13098.

Silver-Catalyzed Trifluoromethylselenylation of Epoxides with [Me_4N][$SeCF_3$]

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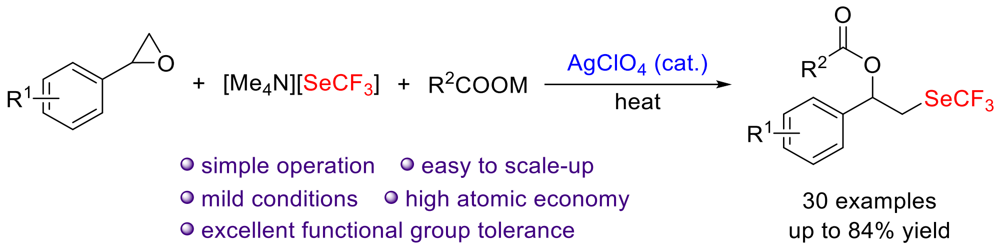
Epoxide is a very useful class of synthetic feedstocks. The nucleophilic ring-opening of epoxide is an important method to obtain difunctionalized organic molecules by a one-pot procedure. In recent years, many ring-opening reactions of epoxides with nucleophilic reagents have been reported,[1] such as amines, thiols, alcohols, phenols, carboxylic acids, azides, cyanides, halogens, trifluoromethoxy, trifluoromethylthio, and others. As a continuing interest in the exploitation of [Me_4N][$SeCF_3$] reagent,[2,3] we has successfully achieved the Ag-catalyzed ring-opening trifluoromethylselenylation and esterification of epoxides with [Me_4N][$SeCF_3$] and aryl or alkyl carboxylates in the presence of $AgClO_4$, which afforded the difunctionalized products in moderate to good yields. This reaction provided a novel strategy for the efficient difunctionalization of epoxides and allowed an atom-economical and concise synthesis of CF_3Se-containing functional molecules.



Keywords: silver-catalyzed, epoxides, trifluoromethylselenylation, difunctionalization

References

1. Ahmad, S.; Yousaf, M.; Mansha, A.; Rasool, N.; Zahoor, A. F.; Hafeez, F.; Rizvi, S. M. A. Synth. Commun. 2016, 46, 1397-1416.
2. Wang, H.-N.; Dong, J.-Y.; Shi, J.; Zhang, C.-P. Tetrahedron. 2021, 99, 132476.
3. Wu, S.; Jiang, T.-H.; Zhang, C.-P. Org. Lett. 2020, 22, 6016-6020.

Organometallic Chemistry of the Perfluorinated Cp* Ligand $[C_5(CF_3)_5]^-$

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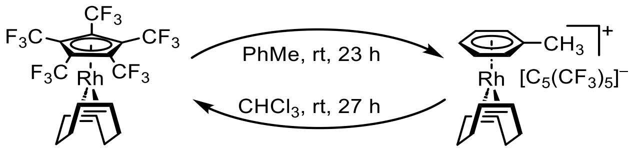
The perfluorinated Cp* anion $[C_5(CF_3)_5]^-$ was first prepared by Lemal in 1980,[1] but its first coordination compound, $[Rh(C_5(CF_3)_5)(COD)]$, was prepared more than 40 years later, due to the low basicity of the ligand.[2] Due to weakened M-Cp interactions, this complex is substitution labile, resulting in unique switchability between being a ligand or a weakly-coordinating anion (Scheme 1).[3-5]

The low basicity and the high oxidative stability of $[C_5(CF_3)_5]^-$ allow the isolation of ionic compounds containing reactive cations which are normally not compatible with cyclopentadienyl anions, e.g. tritylium $[Ph_3C]^+$ or *magic blue* radical cations $[N(C_6H_4Br)_3]^{+}$.[6] Furthermore, coordinating compounds with highly oxidizing metal centers can be isolated, e.g. the first complete series of structurally characterized coinage metal cyclopentadienyl compounds $[(tBu_3P)M(C_5(CF_3)_5)]$ (M=Cu,Ag,Au).[7]

The strongly-electron-withdrawing effect of $[C_5(CF_3)_5]^-$ has also a marked influence on the redox properties of its metal complexes. We have succeeded to prepare the corresponding ferrocene $[Fe(C_5H_5)(C_5(CF_3)_5)]$ with a half-wave potential of $E_{1/2}$= +1.35 V vs. $Fe(C_5H_5)_2$.[8] Even metallocene anions are stabilized by the $[C_5(CF_3)_5]^-$ ligand because they are accessible at much less negative potentials. Correspondingly, the two-fold reduction of the Rh(III) containing rhodocenium cation $[Rh(C_5(CF_3)_5)(C_5(CH_3)_5)]^+$ is possible already with two equivalents of decamethylcobaltocene, resulting in the isolation and structural characterization of $[Co(C_5(CH_3)_5)_2]^+$ $[Rh(C_5(CF_3)_5)(C_5(CH_3)_5)]^-$, being the first example of an ionic compound consisting of metallocene cations and anions with metals in different oxidation states.[9]



Scheme 1. Substitution lability of $[Rh(C_5(CF_3)_5)(COD)]$.

References

[1] Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6633.
[2] Sievers, R.; Sellin, M.; Rupf, S. M.; Parche, J.; Malischewski, M. *Angew. Chem. Int. Ed.* **2022**, *61*, e202211147.
[3] Sievers, R.; Parche, J.; Kub, N. G.; Malischewski, M. *Synlett* **2023**, *34*, 1079.
[4] Parche, J.; Rupf, S. M.; Sievers, R.; Malischewski, M. *Dalton Trans.* **2023**, *52*, 5496.
[5] Kub, N. G.; Sievers, R.; Parche, J.; Malischewski, M. *Chem. Eur. J.* **2024**, *30*, e202400427.
[6] Sievers, R.; Kub, N. G.; Streit, T.-N.; Rupf, S. M.; Malischewski, M. *manuscript submitted*
[7] Sievers, R.; Reimann, M.; Kub, N. G.; Rupf, S. M.; Kaupp, M.; Malischewski, M. *Chem. Sci.* **2024**, *15*, 2990-2995.
[8] Sievers, R.; Kub. N. G.; Streit, T.-N.; Reimann, M.; Thiele, G.; Kaupp, M.; Malischewski, M. *in preparation*.
[9] Kub, N. G.; Sievers, R.; Reimann, M.; Streit, T.-N.; Steinhauer, S.; Schlögl, J.; Kaupp, M.; Malischewski, M. *ChemRxiv* **2025**, https://doi.org/10.26434/chemrxiv-2025-wp0nd

Migratory Allylic C–F Bond Functionalization

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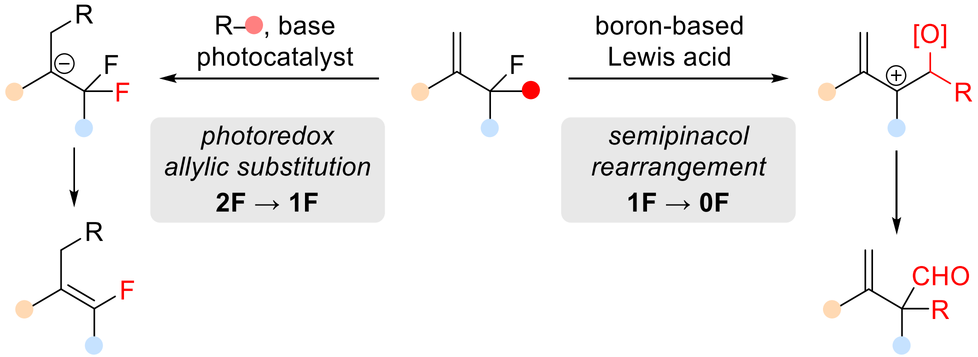
As the C–F bond is the strongest single bond carbon makes with any element, the selective cleavage of this bond in the presence of an abundance of much weaker bonds is a challenge, both from fundamental and synthetically-relevant perspectives. In the case of polyfluorinated starting materials, there are also opportunities for either exhaustive and partial defluorination processes, the latter being more difficult with *gem*-polyfluorinated species as the residual C–F bonds in the product of the first C–F functionalization event are typically weaker than in the starting material.

Our group is particularly interested in partial defluorination processes to attain fluorinated motifs otherwise challenging to prepare, and defluorination reactions that could be leveraged for selective late-functionalization or quick reorganization of the carbon skeleton. In this context, we investigated two transformations involving singular allylic C–F bond functionalization. To this effect, this presentation will cover two reactions investigated by our group that both involve migration. First, the photoredox C–C coupling of allylic difluorides with precursors of carbon-centred radicals will be discussed. In this case, C–F bond cleavage from a β,β-difluorinated carbanion is the termination event, and products are monofluoroalkenes. Second, defluorinative semipinacol rearrangements triggered by boron-based Lewis acids will be highlighted. It has been demonstrated computationally that fluoride abstraction to produce an allylic carbocation is the initiation event, ultimately affording skipped enones as products after a 1,2-shift.



Scheme 1. Defluorinative functionalization of allylic fluorides involving migration of the alkene (photoredox allylic substitution) or the 1,2-shift of a group vicinal to fluorine (semipinacol rearrangement).

Synthetic Approach to CF_3-Alkenyl Derivatives of Amino Acids

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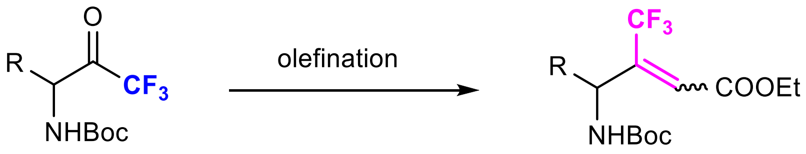
Fluorinated organic compounds have many favourable and unique physicochemical and biochemical properties that play a key role in many current fields of interest e.g. materials engineering, agrochemistry as well as in the pharmaceutical industry.[1]

Peptidomimetics are compounds derived from peptides obtained by structure modification using unnatural amino acids and/or conformational restraints. Modified fluorinated amino acids are of great interest as the building blocks for the preparation of peptidomimetics.

Herein we would like to report synthetic approaches to trifluoromethylated analogues of amino acids bearing olefinic moiety. We've been studying the synthetic routes for the preparation of analogous of amino acids bearing trifluoromethylated olefinic moiety, using trifluoromethylated ketones as starting material and $TMSCF_3$ (Ruppert-Prakash reagent). Additionally, molecular docking of the affinity of synthetic molecules were done in order to predict their biological activity as inhibitors of enzymes. Our focus aims specifically on the inhibitors of Cathepsin C (dipeptidyl peptidase I) which is crucial for the activation of various degradative enzymes that are associated with tissue damage in inflammatory diseases. Therefore, cathepsin C inhibitors may serve as promising therapeutic options for treating conditions such as chronic obstructive pulmonary disease and cystic fibrosis.



Scheme 1. General scheme for the synthesis of CF_3-alkenyl derivatives

References

[1] R. Filler, Y. Kobayashi, L. M. Yagupolskii, *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*; Elsevier: Amsterdam, **1993**.

PARALLEL SESSION VI

Contaminants of Emerging Concern

Supramolecular Architectures and Hydrogels Based on Fluorinated Amino Acids

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Fluorination of organic molecules is gaining a prominent role in medicinal chemistry and materials science, since it is able to alter their physical and chemical properties, and affects their supramolecular chemistry. In particular, the well-known correlation between conformation and function existing in amino acids (AA), peptides, and proteins makes fluorination a key strategy for controlling their assembly modes.[1]

Fluorinated non-natural amino acids (F-AA) can self-assemble into peculiar supramolecular structures, and often show an improved tendency to form fibrils, and gels therefrom. We recently investigated a crystal engineering-based approach for obtaining multicomponent F-AA hydrogels with tuneable strength and properties, by mixing them with suitable partner molecules. Our studies proved the matching between the driving noncovalent interactions in crystals and hydrogels, as shown by the exemplary case of *N*-Fmoc-pentafluoro-L-phenylalanine (**1**, Fig. 1). The choice of suitable partners endowed with biological activity (drugs, vitamins, etc.) could be exploited for their encapsulation and sustained release in biomedical applications.[2]

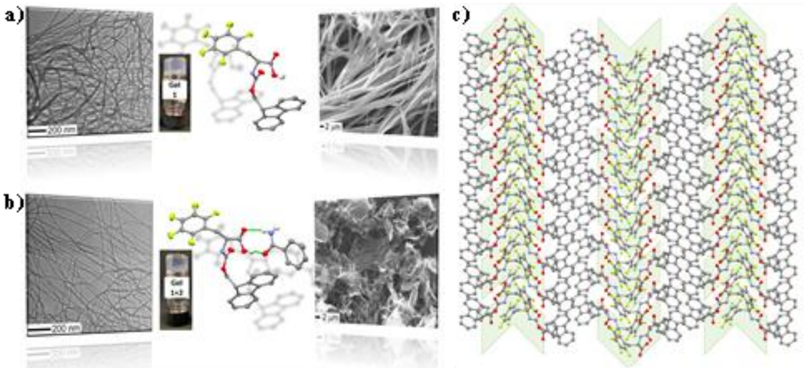

Figure 1. Supramolecular hydrogels of Fmoc-pentafluorophenyl-alanine (**1**): a,b) TEM and SEM images; c) crystal packing of **1**·**2** supramolecular complex.

References

[1] Veronese, E.; Metrangolo, P.; Dichiarante, V. *Chem. Eur. J.*, **2024**, *30*, e202400617.
[2] Veronese, E.; Pigliacelli, C.; Bergamaschi, G.; Terraneo, G.; Dichiarante, V.; Metrangolo, P. *Chem. Eur. J.*, **2023**, *29*, e202301743.

Acknowledgements: V.D. and S.G. acknowledge the project "Probing and simulating the attosecond dynamics of halogenated amino acids", MUR PRIN 2022, project n. 2022WZ8LME (CUP D53D23002920006), funded by the European Union – Next Generation EU.

Complete Mineralization of Lithium Bis(pentafluoroethanesulfonyl)imide and Related Electrolyte Fluorochemicals Using Superheated Water

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Lithium bis(pentafluoroethanesulfonyl)imide, Li[N($SO_2C_2F_5$)$_2$], has been widely used as an electrolyte component in rechargeable lithium-ion batteries, lithium batteries, lithium−air batteries, and all-solid-state lithium batteries. This is due to its exceptional thermal and chemical stability, as well as its outstanding electrochemical properties, including high ionic conductivity, a wide electrochemical window, excellent cycling performance, and strong corrosion resistance. Li[N($SO_2C_2F_5$)$_2$] is currently added to the water-in-salt electrolytes used in aqueous lithium-ion batteries to expand the potential window and reduce manufacturing difficulties by improving the compatibility of the electrolyte with water and air, which increases the battery safety [1,2]. While Li[N($SO_2C_2F_5$)$_2$] contributes to the safety of such batteries, it falls into the category of per- and polyfluoroalkyl substances (PFASs). Nowadays, the European Chemicals Agency plans to restrict all PFASs by 2030.Under these circumstances, waste-treatment technologies that afford complete decomposition of Li[N($SO_2C_2F_5$)$_2$] are needed. Incineration is an option to treat such fluorochemicals including fluoropolymers [3]. However, high temperatures are needed to cleave the strong carbon–fluorine bonds, and HF gas is formed, which damages the firebricks of incinerators. If fluorine atoms in such fluorochemicals could be transformed into fluoride ions (F^-) (that is, mineralization) by means of an environmentally benign technique, the F^- ions could be reacted with calcium hydroxide to form calcium fluoride, which mineral is fluorspar, the raw material for all fluorinated chemicals. Superheated (or subcritical) water is liquid water at temperatures between 100 and 374 °C (water's critical temperature). Reaction using this water is recognized as an environmentally benign technique because it has been shown to have a smaller environmental impact than pyrolysis in the recycling of non-metallic component from electronic waste.

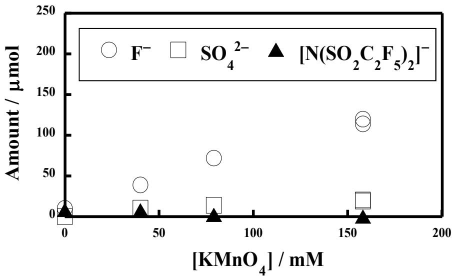

Figure 1. Initial $KMnO_4$ concentration dependence of Li[N($SO_2C_2F_5$)$_2$] decomposition in superheated water. Molar amounts of [N($SO_2C_2F_5$)$_2$]$^-$, F^-, and SO_4^{2-} in the reaction solutions [4].

Here, we demonstrate the complete mineralization of Li[N($SO_2C_2F_5$)$_2$] using superheated water. We also applied this approach to two potassium salt analogues–one containing [N($SO_2C_4F_9$)$_2$]$^-$ and one featuring the cyclic [N(SO_2CF_2)$_2CF_2$]$^-$–both of which are used as electrolytes and in other applications.

References

[1] Xie, J.; Liang, Z.; Lu, Y.-C. *Nat. Mater.*, **2020**, 1*9*, 1006–1011.
[2] Yen, D.; Lin, C.-H.; Sprouster, D. J., Zheng, X.; Xiao, X.; Lee, W.-K.; Ge, M.; Chen-Wiegart, Y. K. *ACS Mater. Lett*. **2023**, *5,* 1466–1475.
[3] Ameduri, B.; Hori, H. *Chem. Soc. Rev*. **2023**, *52*, 4208–4247.
[4] Hori, H.; Okamura, K.; Suzuki, K.; Biermann, M. *ACS Omega* **2024**, *9*, 22398–22409.

Occurrence, Distribution and Fate of Fluorine during Phosphate ore Processing

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Considering the significant decline in global fluorspar reserves, the recycling of fluorine compounds from industrial waste, end-of-life materials, and mining by-products is emerging as a promising approach to mitigate environmental impacts. To meet the growing market demand for fluorine compounds as well as to achieve the long-term management of fluorine resources, phosphate rocks and their derivatives have been identified as a possible source of fluorine. However, the exact occurrence and distribution of fluorine during phosphate ore processing are not yet thoroughly understood. This study was conducted to investigate the distribution, occurrence modes, and release rate of fluorine in Moroccan phosphate as it undergoes the beneficiation process. To do so, phosphate rock samples were analyzed using a multi-analytical approach, combining mineralogical, chemical characterization through ICP-OES, XRD, F-ISE measurements, and Pearson correlation analysis for inter-element correlation. Calcination, digestion, and vacuum evaporation were also used to study the fate of fluorine. The results highlighted that fluorine in phosphate rock mainly exists in a carbonate-bound form as fluorapatite and CaF_2, with a positive correlation to the main components of fluorapatite. By digestion with sulfuric acid and recycled dilute phosphoric acid, the distribution of fluorine in phosphoric acid, phosphogypsum, and the gaseous phase were found to be 12.94%, 31.96%, and 55.10%, respectively. Furthermore, vacuum evaporation of Wet Phosphoric Acid at conditions of 80°C and 120 mmHg resulted in the release of 56.64% of total fluorine as HF and SiF4, thereby increasing the concentration of fluorine in the environment. Consequently, most modern plants are equipped with efficient scrubbing systems capable of removing over 99% of the F-gases, generating a huge quantity of fluorosilicic acid, which is considered a potential source of fluorine-containing compounds used in various applications, from industry to medicine. Finally, our work provides insights into the occurrence and distribution of fluorine in the phosphate industry for the development of sustainable fluorine valorization techniques, which require ongoing research and development efforts.

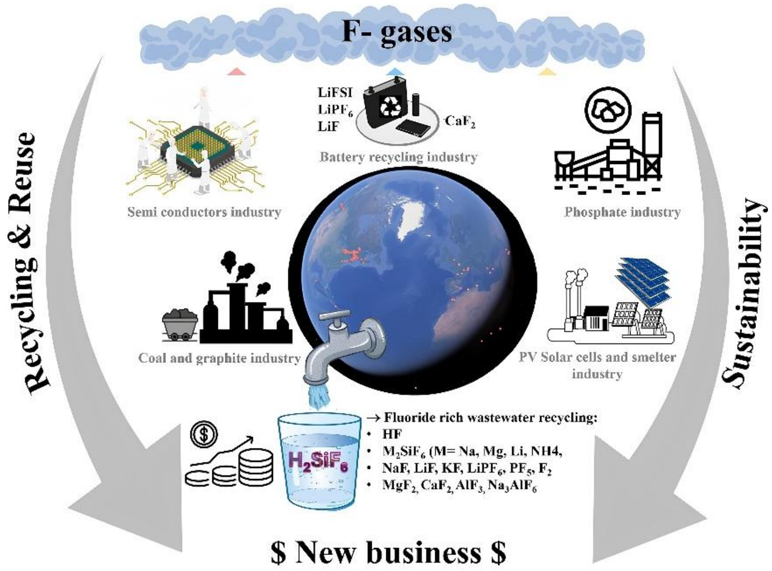

Figure 1. Schematic illustration of anthropogenic sources of fluorine

References

[1] Bingxian Peng, Zhen Ma, Yongbo Zhu, Lixia Tang, Minerals Engineering, 188,2022, 107843, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2022.107843.

Organocatalyzed Synthesis and Depolymerization of Fluorinated Polysiloxanes, a Route to their Chemical Recycling

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Polysiloxanes such as polydimethylsiloxanes (PDMS) or polytrifluoropropylmethylsiloxanes (PTFPMS) are outstanding polymers, which after formulation and crosslinking, can be employed as high performance elastomers in various fields such as automotive or aeronautics.[1] Anionic ring opening polymerization (AROP) of cyclosiloxanes, using acid catalysts, hydroxyde initiators or organolithium compound lead to linear functional polysiloxanes, but with relatively high dispersity or requires the handling and storage of moisture sensitive compounds to achieve narrow molar mass distribution. Efficient and less sensitive organocatalysis for AROP performing under mild and easy conditions and leading to high molar mass and low dispersity polymers (Đ <1.1) is thus of high interest. Inspired by the work of Fuchise et al.,[2,3] this contribution reports the AROP of cyclosiloxanes catalyzed by the commercially available, cost-effective, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Careful choice of initiators and reaction conditions allows the controlled polymerizations and copolymerizations of a variety of cyclosiloxanes including the highly reactive trifluoropropylmethyltricyclosiloxane, and affords well-defined functional copolymers. This contribution will also show how TBD can be used to depolymerise fluorinated polysiloxane and open a route to their chemical recycling.

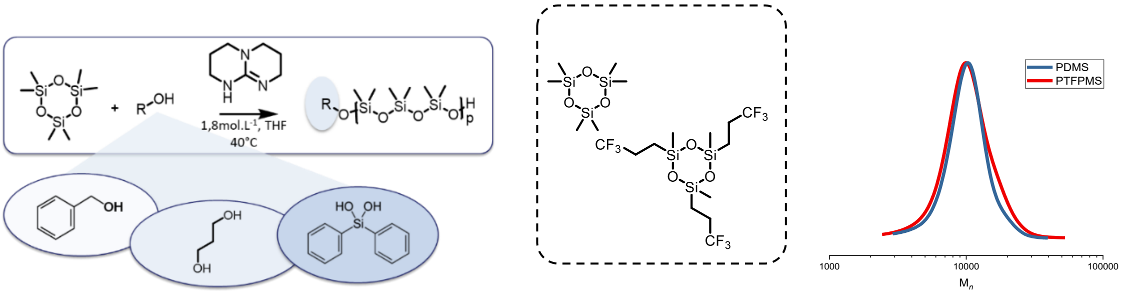

Figure 1. Organocatalyzed AROP of hexamethyltricylosiloxanes (D_3) and trifluoropropylmethylcyclotrisiloxane (F_3).

References

[1] Jones, G. R.; Ando, W.; and Chojnowski, J. *Silicon-Containing Polymers*, Springer Netherlands, **2000**, 3–17.
[2] Fuchise, K.; Igarashi, M.; Sato, K.; Shimada, S. *Chem. Sci.*, **2018**, 9, 2879–91.
[3] Fuchise, K.; Kobayashi, T.; Sato, K.; Igarashi, M. *Polym. Chem.*, **2020**, 11, 7625-7636.

Innovative Bifunctional Siloxane and their Potential Application

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Biological corrosion is the term used to describe the unwanted deposition and growth of all types of microorganisms, mainly fungi, bacteria and algae. It is a multi-step and complex process that leads to the destruction of materials on which this deposition and growth has taken place in the form of a biofilm. This phenomenon not only causes technological problems, but can also have harmful effects on human health. This phenomenon is most often discussed in the context of building materials such as bricks, concrete, roof tiles, glass and wood. Recently, the group of materials with amphiphilic properties has become of increasing interest in the global search for materials with specific properties [1-2]. Compounds with amphiphilic properties are very dynamically developing, multifunctional, because they are a compilation of chemical, biological and physical research. Their specific structure makes them surface active and they are used in many industries [3-5]. This presentation will describe the synthesis of amphiphilic organosilicone compounds and their application as protective coatings against algae for building materials. Bifunctional siloxanes were designed to contain hydrophobic (fluoroalkyl) and hydrophilic (polyether) chains in their structure. The structure of the siloxane backbone makes the compounds permeable to vapors and gases, which is crucial for protecting buildings and building materials. The coating allows free air circulation while providing hydrophobicity due to the presence of fluoroalkyl groups. The presence of polyether groups with a terminal hydroxyl group allows the active ingredient to be permanently bound to the substrate. It should be noted that the use of amphiphilic siloxanes as coatings to protect against the occurrence of biological corrosion is very innovative. The biocidal effect is due to the structure of the siloxane compound and appropriately selected functional groups, rather than the addition of a harmful biocide. It is therefore an environmentally friendly solution.

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References

[1] Kashapov, R., Gaynanova, G., Gabdrakhmanov, D. *International Journal of Molecular Science*, **2020**, *21*, 6961.
[2] Ghosh, S., Ray, A., Pramanik, N. *Biophysical Chemistry*, **2020**, 265, 106429.
[3] Al-Sakkaf, M.A., Onaizi, S.A. *Fuel*, **2024**, *361*, 130604
[4] Guazzelli, E., Martinelli, E., Pelloquet, L., Briand, J-F., Margaillan, A., Bunet, R., Galli, G., Bressy, C. *BIOFOULING*, **2020**, 36, 378.
[5] Adamopoulos, F.G., Vouvoudi, E.C., Achilias, D.S., Karapanagiotis, I. *Heritage* **2021**, *4*, 2668.

Impacting High Pressure Structural Transition of Alkali Metal Hexafluorides

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Pressure-induced structural and electronic changes with the application of high-pressure (>1GPa) opened numerous novel properties in the past decades. One example is the transition of $MgSiO_3$ in the perovskite to postperovskite structure ($CaIrO_3$-type) occurring in the mantle's D" region, unfortunately with extreme conditions possibly difficult to reproduce in laboratory (125 GPa and 2500 K). The $NaM^{2+}F_3$ fluorides (M = Ni, Co, Mg, Mn, and Zn) received attention as they can be considered as robust analogous compounds that also undergo perovskite (Pv) to postperovskite (pPv) transitions, but at much lower conditions (10−20 GPa and 800−1473 K).[1] Following this result, reducing the pressure conditions of a structural modification in fluorides can be a challenge to overcome. A possible strategy was found with the phase relations of $Li_2M^{4+}F_6$ under high pressure conditions being strictly correlated with the ionic radius of the M^{4+} tetravalent cation in six-fold coordination (r_{Ti4+} = 0.605 Å, r_{Mo4+} = 0.650 Å and r_{Zr4+} = 0.720 Å) : Li_2TiF_6 and Li_2MoF_6 were stabilized with the Li_2ZrF_6-type structure by synthesis under 7.7 GPa and 3 GPa, respectively.[2] An extension was made with the cryolite β-Li_3VF_6. A high pressure form (HP-Li_3VF_6) could be observed as evidenced by *in situ* Synchrotron X-Ray Diffraction (SXRD) and Raman Spectroscopy in Diamond Anvil Cell (DAC) around 3 GPa at ambient temperature (Figure 1). A precursor modification was then investigated with the comparison between microsized and nanosized β-Li_3VF_6 and also demonstrates the possibility to trigger the structural transition at "lower" high-pressure with nanosized precursors.

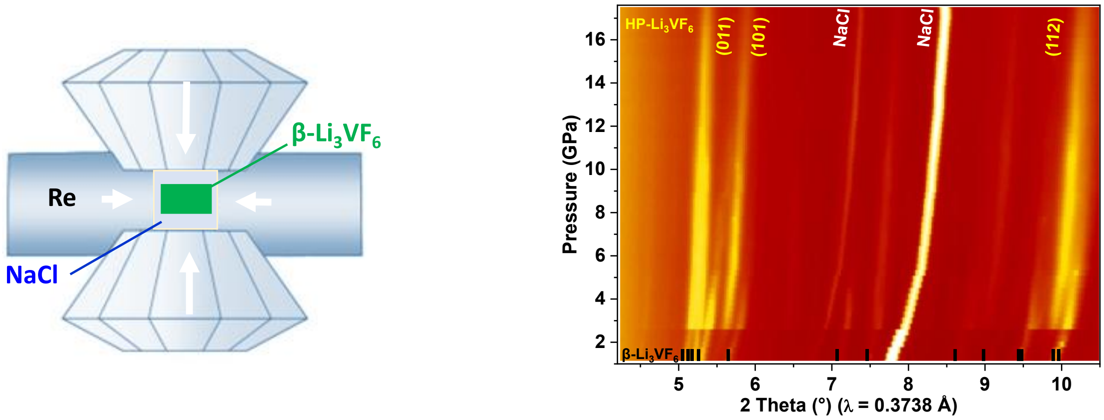

Figure 1. Diamond Anvil Cell (left), *In situ* SXRD of cryolite β-Li_3VF_6 under high pressure in DAC configuration (right).

References
[1] Shirako, Y.; Shi, Y. G.;. Aimi, A.; Mori, D.; Kojitani, H.; Yamaura, K.; Y. Inaguma, Y.; Akaogi, M.; *J. Solid State Chem.* **2012** *191*, 167–174.
[2] Inaguma, Y.; Oyanagi, M; Ueda, K; *Inorg. Chem.* **2022** *61* (3), 1728-1734.

Synthesis of α-Fluoroalkylated Pyridines and Pyrimidines via Direct Fluorination with NFSI

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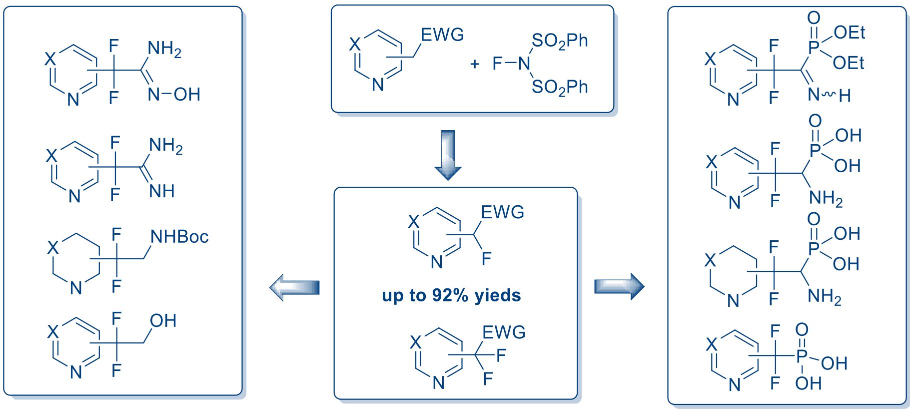
Pyridines and pyrimidines are essential scaffolds in medicinal chemistry and biochemistry, with pyridine and piperidine motifs ranking among the most frequently encountered nitrogen-containing heterocycles in FDA-approved drugs. Meanwhile, the incorporation of (poly)fluoroalkyl groups into heterocyclic systems has become a well-established strategy in drug design due to the enhanced lipophilicity, metabolic stability, and favorable physicochemical properties these groups confer.

Current methods for synthesizing fluoroalkylated azines fall into two general categories [1]. The first involves the introduction of pre-formed fluorinated fragments - typically via cross-coupling reactions with fluorine-containing building blocks. The second comprises direct fluorination approaches, including deoxofluorination or electrophilic fluorination using N–F reagents, which allow for the installation of fluorine atoms directly onto azine frameworks, offering greater synthetic versatility.

This presentation will highlight our recent progress in the selective electrophilic mono- and gem-difluorination of pyridinyl- and pyrimidinylacetic acid derivatives, including esters, nitriles, and phosphonates - using NFSI (N-fluorobenzenesulfonimide).



X = CH, N; EWG = CO_2Et, CN, $P(O)OEt_2$

We will also discuss the synthetic utility of the resulting mono- and α,α-difluorinated pyridinyl- and pyrimidinylacetic acid derivatives as key intermediates for generating pharmacologically relevant compounds bearing difluoromethylene-substituted pyridinyl and pyrimidinyl motifs. Examples include amines, amidines, oxadiazoles, aminopiperidines, and aminophosphonic acids.

References

[1] Shavrina O.M.; Rassukana Yu. V.; Onys'ko P. P. *Curr. Org. Synthesis,* **2024**, *21*, 1053-1074.

Amine-functionalized Fluoroarenes for Energy and Environmental Applications

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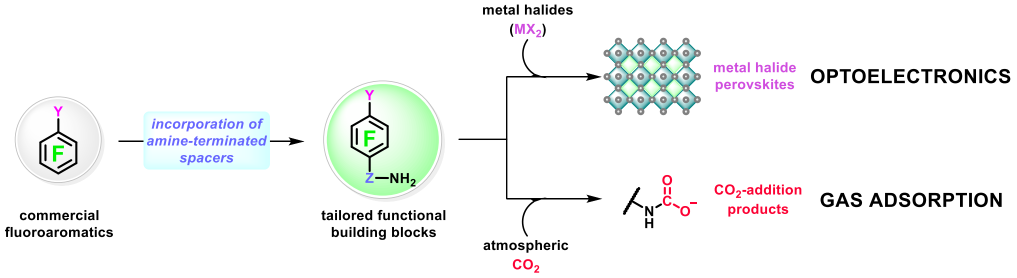
Fluoroarenes have a rich chemistry allowing their derivatization towards tailor-made functional building blocks. The presence of fluorine atoms allows to tune the hydrophobicity of the desired compounds, as well as to take advantage of their electronegativity towards the control of their supramolecular assemblies. In this work we explored a series of amine-functionalized Y-fluoroarenes (Y= H, halogen). The Y substituent, ranging from hydrogen to halogen atoms, facilitates an additional control on the supramolecular assembly through additional fluorine-fluorine interactions, fluorine-halogen interactions and halogen bonds. [1] Overall, it is a molecular library for versatile applications. Herein, we focus in two main technology branches: gas adsorption and optoelectronics. In the form of free amines, we studied the spontaneous carbon dioxide (CO_2) capture from atmospheric air and the impact of the molecular design on CO_2 chemisorption. [2] The developed amine-functionalized Y-fluoroarenes in the form of ammonium halides, can have been effectively used as cations for the synthesis of semiconducting low-dimensional hybrid organic-inorganic metal halide perovskites. [3] Crystallographic and physical properties characterization provide meaningful insights into materials design and structure-properties relation.



Scheme 1. Schematic illustration of the implementation of commercially available fluoroaromatics towards the development of tailored functional building blocks for optoelectronic and gas adsorption technologies.

Acknowledgments

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References

[1] Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati; T., Priimagi, A., Resnati, G; Terraneo, G., *Chem. Rev.*, **2016**, *116*, 2478–2601.
[2] Chen, H.; Yang, Z.; Do-Thanh, C.L., Dai, S. *ChemSusChem*, **2020**, *13*, 6182-6200.
[3] a) Metrangolo, P.; Canil, L.; Abate, A.; Terraneo, G; Cavallo, G. *Angew. Chem. Int. Ed.* **2022**, *61*, e202114793-e202114800. b) Stergiou, A.; Leccioli, L.; Ricci, D.; Zaffalon, M.; Brovelli, S.; Baldelli Bombelli, F.; Terraneo, G.; Metrangolo, P.; Cavallo, G. *Angew. Chem. Int. Ed.*, **2024**, *63*, e202408570.

Managed Aquifer Recharge: A New Frontier for Addressing Emerging Contaminants

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Chemicals play a vital role in modern society, yet many, including long-standing compounds and emerging contaminants (ECs) such as PFAS, pesticides, and pharmaceuticals, remain largely unregulated or insufficiently studied. These persistent pollutants accumulate in the environment, threatening human health and ecosystems, particularly through surface and groundwater contamination. To address these challenges, a multidisciplinary approach is crucial, especially for understanding their behaviour in Managed Aquifer Recharge (MAR). At the same time, regulatory efforts must strike a balance between minimizing risks and preserving the essential use of key chemicals.

MAR2PROTECT project addresses the challenges of groundwater contamination caused by climate and global change through a holistic approach. It focuses on developing innovative technologies and tools supported by Artificial Intelligence to monitor and prevent contamination using real-time data from sensors placed at high-risk locations among others, to inform the deployment of these technologies. The NOVA FCT team is leading the development of advanced adsorption processes for the removal of PFAS and pharmaceuticals and a real-time PFAS monitoring sensor in collaboration with IT from Aveiro. These solutions aim to minimize one of the entry points for ECs by implementing quaternary effluent treatment in WWTPs and enabling its use in MAR.

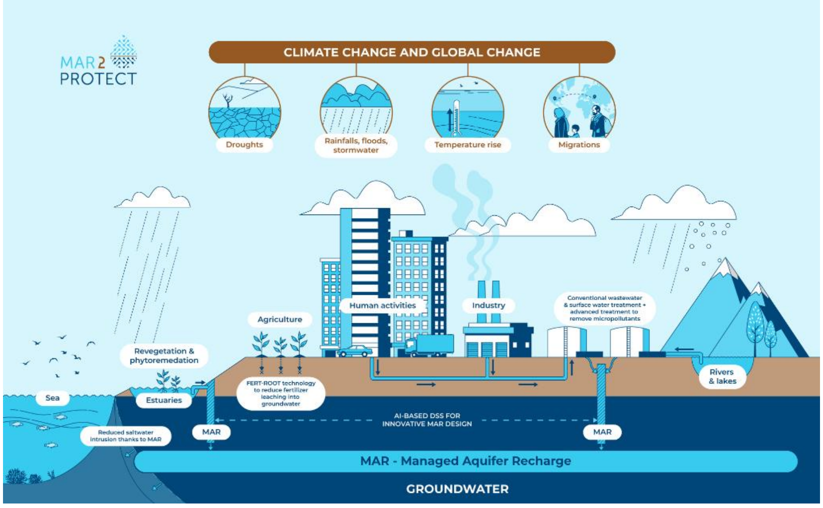

Figure 1. MAR2PROTECT approach to prevent groundwater contamination from the impacts of global and climate change (source: https://mar2protect.eu/)

References

[1] Mumberg, T., Ahrens, L., & Wanner, P. (2024). Managed aquifer recharge as a potential pathway of contaminants of emerging concern into groundwater systems – A systematic review. Chemosphere, 364. https://doi.org/10.1016/j.chemosphere.2024.143030

PARALLEL SESSION VI

Organic Chemistry

Chemical Recycling of Fluorocarbons by Transfer Fluorination

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The production of fluorochemicals is currently achieved through a linear manufacturing process starting from fluorspar (CaF_2). While fluorochemicals improve our quality of life, there is increasing concern over their negative impact on health and the environment. Here we report an approach to preparing fluorine-containing molecules through recycling.[1-2] Treatment of hydrofluorocarbons with a base results in rapid defluorination to produce anhydrous potassium fluoride. The scope of fluorochemicals that can be recycled includes industrially relevant hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs), fluoroethers – including anaesthetics and battery additives, poly(fluoroalkyl) substances (PFAS) including per(fluorooctanoic) acid (PFOA), along with fluorinated polymers such as poly(vinylidene difluoride) (PVDF). The in situ generated anhydrous potassium fluoride harvested from these materials can then be used to prepare a wide range of organic and inorganic molecules.

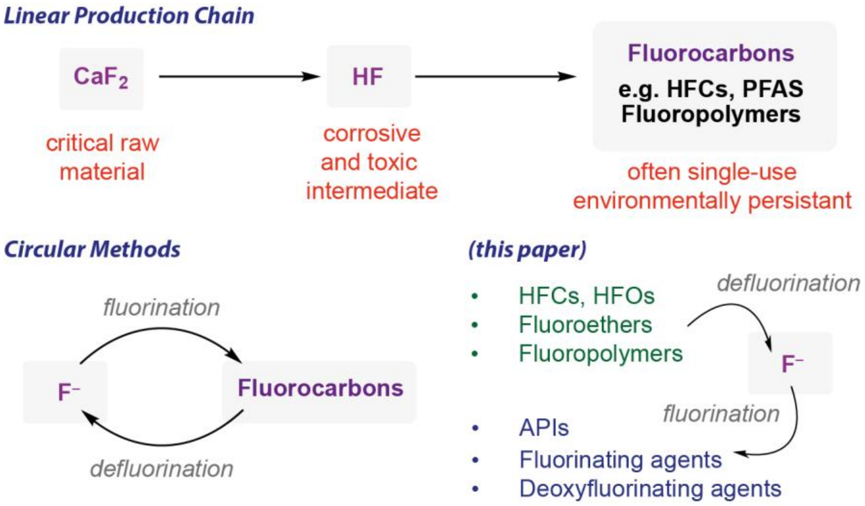

Figure 1. Linear and circular production chains for fluorocarbons.

References

[1] S. E. S. Farley, D. Mulryan, F. Rekhroukh, A. Phanopoulos, Mark R. Crimmin, *Angew. Chem. Int. Ed.* **2024**, *63*, e202317550.
[2] D. J. Sheldon, J. M. Parr, M. R. Crimmin, *J. Am. Chem. Soc.* **2023**, *145*, 10486–10490.

The Role of Electrostatic Non conventional Hydrogen Bonding Interactions in Organofluorine Compounds

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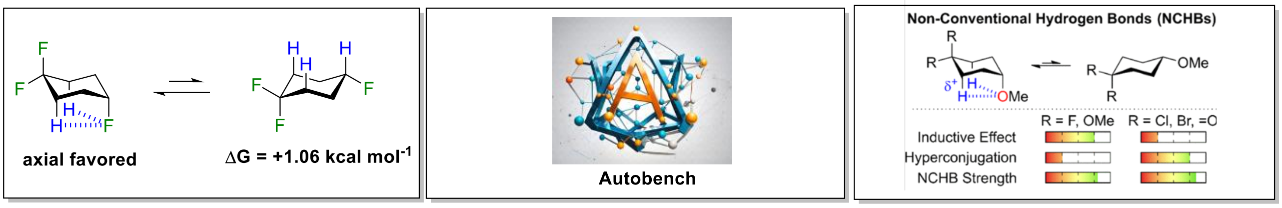
Theoretical calculations, on the basis of density functional theory (DFT) and *ab initio* methods, have been used in our group to investigate the conformational preferences of organofluorine compounds and the underlying factors governing their stability. These calculations have also been used to study the effects of substituents and solvents on the conformational behavior and experimental spectroscopic parameters of organofluorine compounds. In addition to conformational studies, NMR spectroscopy and theoretical calculations were used to investigate the nature of non-covalent interactions, such as classical and non conventional hydrogen bonding, which play a major role in the properties and reactivity of organofluorine compounds. In particular, the use of ^{1}H and ^{19}F NMR spectroscopy and DFT calculations has allowed for the characterization of such interactions and their spin-spin coupling constants transmission pathways.
This work will focus on the recent publications from our lab on theoretical calculations and NMR and infrared spectroscopy applications to provide insights into the geometry, noncovalent interactions and spectroscopic parameters of organofluorine compounds, which encompasses a range of topics, as how good is organic F as a H-bond acceptor, the challenges of calculation of spin-spin coupling constants involving F atoms, stereoelectronic effects involving the fluorine atom and non conventional H-bonds.



Scheme 1. Representative examples of works that will be covered in the presentation

References

[1] He, M.; Piscelli, B. A. ; Cormanich, R. A.; O'Hagan, D. J. Org. Chem. **2024**, *89*, 4009-4018.
[2] Cormanich, R. A.; da Silva, G. D. *J. Chem. Inf. Model.* **2024**, *64*, 3322–3331.
[3] Cariello, G.; Zeoly, L. A.; Piscelli, B. A.; Lectka, T.; Cormanich, R. A. *Chem. Comm.* **2023**, *59*, 14661-14664.

Recent Advances in the Synthesis of Pentafluorosulfanylated Molecules

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Since its discovery, the pentafluorosulfanyl group (SF_5) has been attracting its share of attention in organic chemistry. Considered as a “super CF_3”, the SF_5 group has interesting properties including, amongst others, a high lipophilicity and a strong electron-withdrawing capacity.[1] These characteristics make it a substituent of choice in medicinal chemistry, agrochemistry and material sciences.[2] In that context, the development of novel synthetic methods for the preparation of pentafluorosulfanylated molecules in an important objective.[3]

This presentation will describe some recent results towards the synthesis of SF_5-containing molecules starting from SF_5Cl (Figure 1).[4]

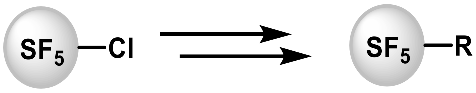

Figure 1. Synthesis of pentafluorosulfanylated molecules starting from SF_5Cl.

References

[1] Savoie, P. R.; Welch, J. T. *Chem. Rev.* **2015**, *115*, 1130−1190.

[2] For reviews on the use of pentafluorosulfanylated molecules in these fields, see (a) Sowaileh, M. F.; Hazlitt, R. A.; Colby, D. A. *ChemMedChem* **2017**, *12*, 1481–1490. (b) Chan, J. M. W. *J. Mater. Chem. C* **2019**, *7*, 12822–12834. (c) Sani, M.; Zanda, M. *Synthesis* **2022**, *54*, 4184–4209. (d) Kordnezhadian, R.; Li, B.-Y.; Zogu, A.; Demaerel, J.; De Borggraeve, W. M.; Ismalaj, E. *Chem. Eur. J.* **2022**, *28*, e202201491.

[3] Selected recent reviews: (a) Das, P.; Tokunaga, E.; Shibata, N. *Tetrahedron Lett.* **2017**, *58*, 4803–4815. (b) Haufe, G. *Tetrahedron* **2022**, *109*, 132656. (c) Popek, L.; Nguyen, T. M.; Blanchard, N.; Cahard, D.; Bizet, V. *Tetrahedron* **2022**, *116–118*, 132814.

[4] For recent contributions of our group in this area, see (a) Paquin, P.; DeGrâce, N.; Bélanger-Chabot, G.; Paquin, J.-F. *J. Org. Chem.* **2024**, *89*, 3552−3562. (b) Mastalerz, V.; Verret, L.; Paquin, J.-F. *Eur. J. Org. Chem.* **2024**, *27*, e202400956. (c) Verret, L.; Burchelle-Reyes, K.; Morin, J.-F.; Paquin, J.-F. *J. Fluorine Chem.* **2025**, *232*, 110387.

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Experimental and Theoretical Study of Difluorobenzimidazoles

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Significant part of fluorinated compounds applied as drugs or agrochemicals contain fluoroarene moiety. Introduction of fluorine into both activated and deactivated arene rings thus still represent a reasonable challenge. Among the reagents able to transform directly phenols into fluoroarenes, difluoroimidazoles and difluoroimidazolidines play a distinctive role. First, Hayashi et al. reported synthesis and deoxyfluorination capabilities of a new class of reagents 2,2-difluoro-1,3-dimethylimidazolidine (**1**, **DFI**, Figure 1).[1] While 4-nitrophenol was deoxyfluorinated in moderated yield, non-activated phenols proved to be unreactive forming only stable corresponding uronium hydrogen difluoride. Much higher efficiency showed **Phenofluor**™ reagent, 1,3-bis(2,6-diisopropylphenyl)-2,2-difluoro-2,3-dihydro-1*H*-imidazole (**2**), which was able to convert both activated and non-activated phenols to the corresponding fluoroarenes in high yields.[2] Just recently, analogous mesitylene based difluoroimidazolidine **3** (**SIMesF2**) reagent was reported, but no reaction with phenols was successful.[3] Both latter reagents were formed through the corresponding carbenes, making their recycle impossible. We hence developed the synthesis of analogous **BMIF2** reagent **4** through the corresponding easily accessible benzimidazolones, which enables the recycle of the spent reagent (Figure 1). The reagent does not react with unactivated phenols, but gave moderate to poor yields of fluoroarenes with phenols modified with electron-withdrawing groups. For the reaction with 4-nitrophenol, detailed analysis of the NMR spectra disclosed that bis(4-nitrophenyl)ether was formed as the main unexpected side product. Similar behavior was also observed for other activated phenols.

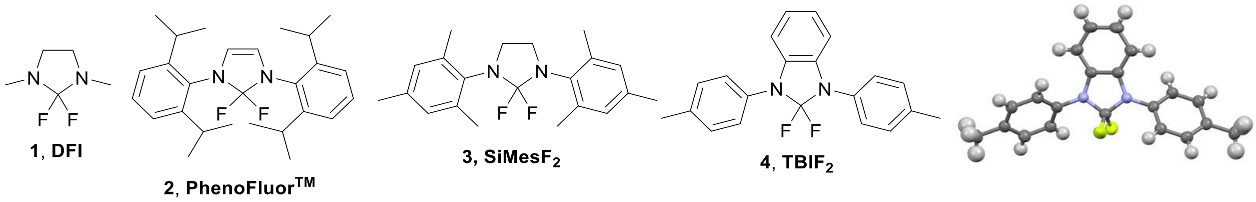

Figure 1. Known difluoroimidazoles and difluoroimidazolidines employed in arene deoxyfluorinations

While the mechanism of fluorination through the key intermediate, fluorophenoxyimidazole, derived from the PhenoFluor™ reagent, was studied in detail by DFT methods, no attention was given to conformational analysis of the above given reagents. We found that higher reactivity of the **PhenoFluor**™ reagent **2** can be attributed to beneficial conformation of the fluorophenoxy intermediate compared to the other reagents.

References

[1] Hayashi, H.; Sonoda, H.; Fukumura, K.; Nagata, T. *Chem. Commun,* **2002**, 1618-1619.
[2] Tang, P.; Wang, W.; Ritter, T. *J. Am. Chem. Soc.* **2011**, *133*, 11482-11484.
[3] Herbstritt, D.; Tomar, P.; Müller, R.; Kaupp, M.; Braun, T. *Chem. Eur. J.* **2023**, *29*, e202301556.

Shelf-Stable Reagent for Radical Pentafluorosulfanylation

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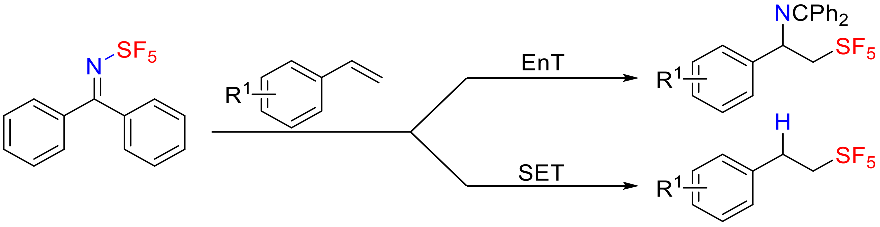
In recent years, fluorinated compounds have gained increasing attention due to their strong lipophilicity and electronegativity, finding applications in pharmaceuticals,[1] agriculture,[2] and materials science.[3] Notably, trifluoromethyl-containing compounds such as Sitagliptin for diabetes, Paxlovid for COVID-19, and Lenacapavir for HIV-1 have been widely used. However, the trifluoromethyl group belongs to the class of perfluoroalkyl and polyfluoroalkyl substances (PFAS), which are highly stable and degrade into trifluoroacetic acid (TFA). TFA is extremely persistent in the environment and accumulates in ecosystems, posing significant ecological risks. In response, the European Union has proposed a "Fluorine Ban", set to take effect in 2027.[4] Given this situation, SF_5 emerges as a promising alternative to the trifluoromethyl group. It exhibits even higher electronegativity and lipophilicity than CF_3, earning the nickname "Super Trifluoromethyl". However, the direct synthesis of SF_5-containing molecules is highly challenging. SF_5Cl is commonly used as an SF_5 reagent,[5] but it is a toxic gas, unstable, and difficult to handle. To address this, we have developed a shelf-stable SF_5 reagent. By reacting NSF_3 with trichloroisocyanuric acid and KF, we obtained Cl_2NSF_5, which, upon reaction with Diazo compounds, yielded a series of N-SF_5 imine derivatives. Moreover, compound Ph_2C=N-SF_5 imine can serve as an SF_5 reagent to react with styrene, selectively producing imino-pentafluorosulfanylated and hydropentafluorosulfanylated compounds via single electron transfer and energy transfer separately (**Scheme 1**). Mechanistic validation experiments have comprehensively elucidated these reaction processes.



Scheme 1. Imino-pentafluorosulfanylated and hydropentafluorosulfanylation of styrene.

References

[1] Britton, R. *et al. Nat. Rev. Methods Primers.* **2021**, *1*, 47.
[2] Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai, N. Shibata, *iScience* **2020**, *23*.
[3] C. Zhang, K. Yan, C. Fu, H. Peng, C. J. Hawker, A. K. Whittaker, *Chem. Rev.* **2022**, *122*, 167.
[4] N. D. Tyrrell, *Org. Process. Res. Dev.* **2023**, *27*, 1422.
[5] P. R. Savoie, J. T. Welch, *Chem. Rev.* **2015**, *115*, 1130.

Tetrafluoropyridyl Groups; Applications in Molecular Functionalisation

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Developing new ways to selectively functionalise compounds has become increasing important in organic synthesis. Allowing diverse libraries of compounds to be accessed through elaboration of a small group of core scaffolds. To achieve selective functionalisation, new reagents are required which can interact with select functional groups whilst leaving others untouched. We have a long-standing interest in the use of perfluorinated aromatics and their interesting properties when it comes S_NAr and displacement chemistries. We have found that compounds such as hexafluorobenzene and pentafluoropyridine can have uses in functionalisation of diverse chemical scaffolds from small molecules to peptides.[1-3] Pentafluoropyridine (PFP) for example is an interesting reagent as not only can it readily react with nucleophiles, but it can also dramatically change the electronics of aromatic systems with its highly electron deficient nature. Due to these properties, we have utilised PFP in a range of functionalisation reactions including modification of peptides, amino acids and asymmetric bi-aryls.[4, 5] Our developed synthetic methodologies allow for easy to conduct and selective modification using cheap commercially available reagents which can be used under mild reaction conditions.

In this presentation a range of applications of pentafluoropyridine in molecular functionalisation will be discussed. This will include work on the selective protection of phenols along with remote regioselective functionalisation of bisphenols. It will also touch on other areas such as modification of biologically relevant scaffolds and molecular derivatisation for single crystal determination.

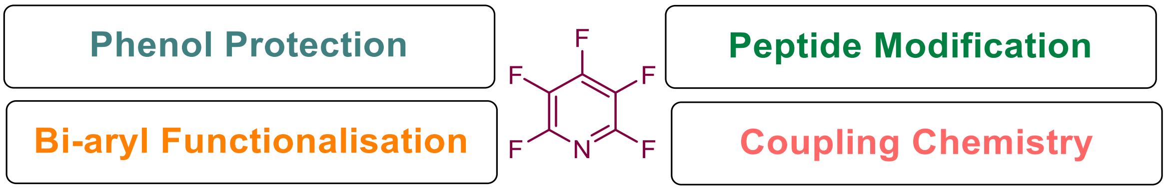

Figure 1. Applications of pentafluoropyridine across organic synthesis

References

[1] Brittain, W. D. G.; Cobb, S. L. *Org Biomol Chem* **2019**, *17* (8), 2110-2115.
[2] Brittain, W. D. G.; Cobb, S. L. *J. Org. Chem* **2020**, *85* (11), 6862-6871.
[3] Gimenez, D.; Mooney, C. A.; Dose, A.; Sandford, G.; Coxon, C. R.; Cobb, S. L. *Org. Biomol. Chem* **2017**, *15* (19), 4086-4095.
[4] Beardmore, L. N. D.; Cobb, S. L.; Brittain, W. D. G. *Org. Biomol. Chem* **2022**, *20* (41), 8059-8064.
[5] Brittain, W. D. G.; Cobb, S. L. *Org. Lett.* **2021**, *23* (15), 5793-5798.

Thionyl Fluoride as a Sulfur(IV) SuFEx Hub for the Efficient Syntheses of Sulfinamides and Sulfinate Esters

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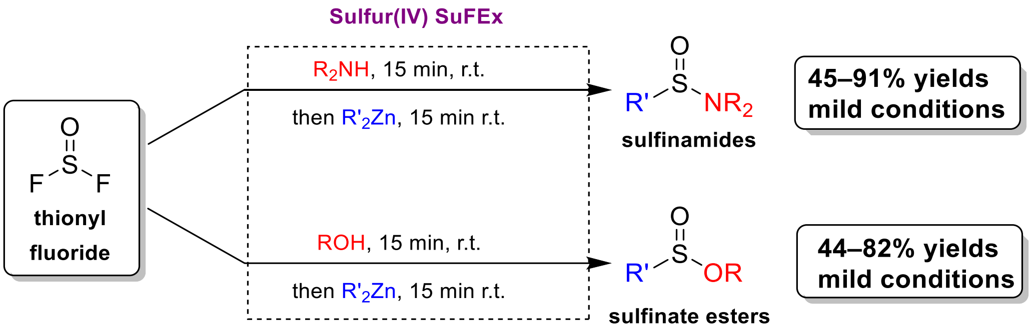
The exploration of Sulfur-Fluoride Exchange (SuFEx) chemistry involving sulfur(VI) fluorides has grown substantially[1] since being developed by Sharpless and co-workers in 2014.[2] It has been widely utilised in a variety of applications[3] as a highly efficient click reaction, along with the simultaneous development of various S(VI) connective hubs for assembling molecules.[1,4] However, SuFEx with the analogous S(IV) fluorides has not been explored in any depth. Only a single published example existed prior to the research discussed herein,[5] and the scope was limited to only heteroatom linkages. This work demonstrates the underexplored reagent thionyl fluoride (SOF_2), as a versatile S(IV) SuFEx hub.[6] Our strategy involves the addition of an alcohol or amine to SOF_2, followed by an organozinc reagent, accessing sulfinamides and sulfinate esters. This is the first time these substrates have been accessed by SuFEx chemistry, the first use of S(IV) SuFEx with organometallic reagents, and only the second ever S(IV) SuFEx publication. The reactions are also rapid, operate under mild conditions, and allow highly modular access to a variety of substrates.



Scheme 1. Sulfur(IV) SuFEx with SOF_2.

Current work involving a new, non-gaseous S(IV) fluoride reagent will also be discussed.

References

[1] Barrow, A. S.; Smedley, C. J.; Zheng, Q.; Li, S.; Dong, J.; Moses, J. E. *Chem. Soc. Rev.*, **2019**, *48 (17)*, 4731–4758.
[2] Dong, J.; Krasnova, L.; Finn, M. G.; Sharpless, K. B. *Angew. Chem.*, *Int. Ed.*, **2014**, *53 (36)*, 9430–9448.
[3] For a review on a representative application involving chemical probes, see: Jones, L. H.; Kelly, J. W. *RSC Med. Chem.*, **2020**, *11 (1)*, 10–17.
[4] For a recently developed such hub, see: Li, B.; Su, K.; Van Meervelt, L.; Verhelst, S. H. L.; Ismalaj, E.; De Borggraeve, W. M.; Demaerel, J. *Angew. Chem., Int. Ed.*, **2023**, *62 (29)*, e202305093.
[5] Downey, K. T.; Mo, J. Y.; Lai, J.; Thomson, B. J.; Sammis, G. M. *Chem. Sci.*, **2023**, *14 (7)*, 1775–1780.
[6] Chappell, W. P.; Favié, M.; Sammis, G. M. *Chem. Commun.*, **2024**, *60 (72)*, 9765–9768.

PARALLEL SESSION VII

Inorganic Chemistry

Exploring Xenon Difluoride Coordination Compounds: From Initial Discoveries to Novel SO_3F^- Anion

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Since the simultaneous discovery of XeF_2 by [1] there has been significant interest in this compound. However, the first coordination compound featuring XeF_2 was discovered much later [2]. To date, numerous coordination compounds with central metal (M= I, II, III) have been synthesized [3]. Typically, the counter anions in these compounds are octahedral AF_6^-, except for tetrahedral BF_4^- and dimeric $V_2O_2F_8^{2-}$, due to the strong oxidative properties of XeF_2 which limit the selection of stable anions. Recently, new advancements have been made with the preparation and characterization of the first coordination compounds incorporating the SO_3F^- anion.

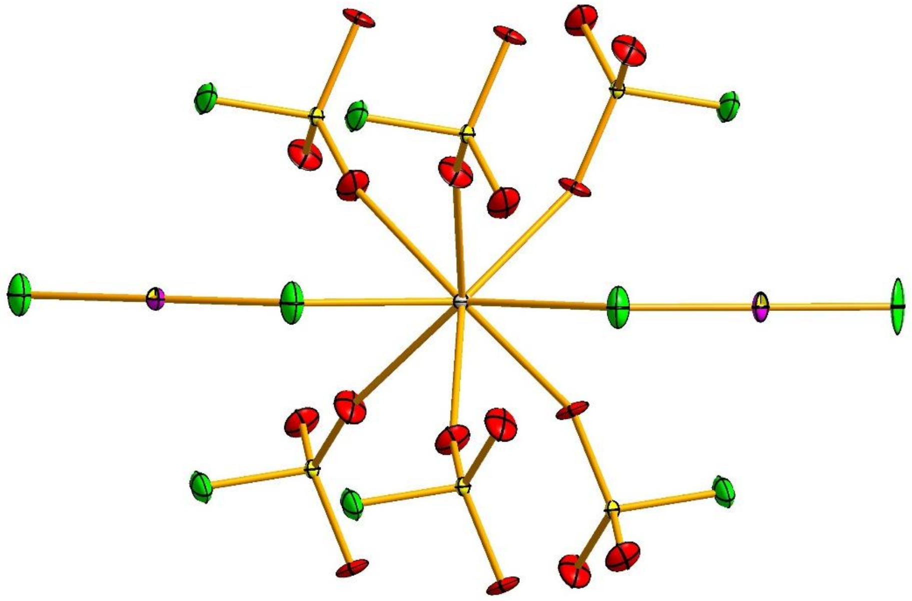

Figure 1. Coordination sphere of Ca in $[Ca_2(XeF_2)_3]_2(SO_3F)_4$.

References

[1] Hoppe, R.; Dähne, W.; Mattauch, H.; Rödder, K.M.; *Angew. Chem. Int. Ed.,* **1962,** *74,* 903; Chernick, C.L.; Claassen, H.H.; Fields, P.R.; Hyman, H.H.; Malm, J.G.; Manning, W.M.; Matheson, M.S.; Quarterman, L.A.; Schreiner, F.; Selig, H.H.; Sheft, I.; Siegel, S.; Sloth, E.N.; Stein, L.; Studier, M.H.; Weeks, J.L.; Zirin, M.H.; *Science,* **1962**, 138136–138.

[2] Hagiwara, R.; Hollander, F.; Maines, C.; Bartlett, N.; *J. Eur, Solid State Inorg. Chem.;* **1991**, *28*, 855–866.

[3] Tavčar, G.; Tramšek, M.*; J. Fluorine Chem.;* **2015**, *174*, 14-21.

Manipulating F···F interactions for metal extractions

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The proliferation of new technology has resulted in a large increase in electronic waste (e-waste) that in some cases are richer in precious metals than virgin ores. However, extracting pure metals from this heterogeneous mixture is challenging. Some of these metals have been defined as energy critical [1] e.g. Nd is important for many applications including magnets for hard-disc drives or wind turbines. Solvent extraction methods have been used to some extent, but there is room for improvement. One method is to design extractant ligands that will coordinate the metal ions in acidic aqueous solutions and here we use long chain fluorinated groups to enhance solubility in the benign solvent $scCO_2$. Some of the extractants we have synthesised are shown in Figure 1a [2]. We have used these to extract a series of precious metals (Ag, Au, Pd, Pt) and lanthanide ions and excellent extractions have been observed (Fig 1b). The nature of the extractable species has been elucidated via small angle X-ray scattering, NMR spectroscopy and binding constants determined. Modifications of the original ligands displays methods to enhance extraction abilities.

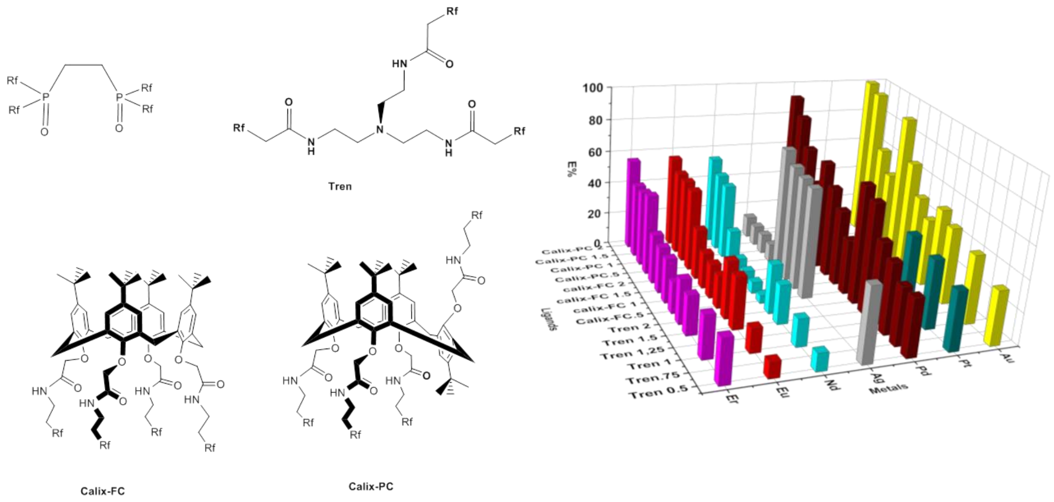

Figure 1. New fluorous ligands (Rf = $(CF_2)_5CF_3$) for extraction of metals (left) and summary of extraction results (right).

References

[1] *Critical Materials Strategy*, US Department of Energy, December **2013**; *Critical raw materials for the EU*, European Commission, June **2010**; *Critical Metals for Future Sustainable Technologies and their Recycling Potential*, United Nations Environment Programme, **2009**.

[2] H. Omorodion, M. Palenzuela, B. Twamley and R. J. Baker, New J. Chem., **2018**, 42, 7956 – 7968; H. Omorodion, B. Twamley, J. A. Platts and R. J. Baker, Cryst. Growth Des., 2015, 15, 2835; R. J. Baker, J. Baker and C. Schulzke, *Gold Bull.*, **2011**, 44, 79; R. J. Baker, T. McCabe, J. E. O'Brien, and H. V. Ogilvie, *J. Fluor. Chem.*, **2010**, 131, 621.

Fluorination by Solid-gas Reaction of High-performance Compounds for Rechargeable Batteries

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Lithium-ion (LiB) batteries are pivotal to modern energy storage systems, powering electric vehicles and many everyday electronic devices. The market for rechargeable lithium batteries is booming as new technological applications demand higher energy densities and advances in storage and safety. From a safety perspective, the nucleation and growth of lithium dendrites can cause the battery to short-circuit when the two electrodes are connected. On the other hand, battery overheating can cause fires or system explosions because liquid electrolytes contain flammable solvents. The development of non-flammable solid electrolytes seems to be the solution to this safety problem, forming a barrier that inhibits the growth of lithium dendrites, thus preventing contact between the two electrodes. [1, 2] Solid electrolytes are becoming increasingly popular in research due to their recent interest in the energy field.

In this symposium, we will present the state of the art of studies carried out to improve the performance of these materials. In particular, we will focus on one of the approaches being explored: fluorination. Fluorination has emerged as a promising technique to optimize the properties of solid electrolytes, especially in terms of ionic conductivity and electrochemical stability. [3,4] Finally, the results of research work carried out on this subject, including the fluorination of a solid electrolyte using xenon difluoride XeF_2, will be presented. The fluorination of two types of materials will be highlighted, a crystalline material and a glass-ceramic material.

References

[1] Zheng, F.; Kotobuki, M.; Song, S.; Lai, M. O.; Lu, L. *J. Power Sources* **2018**, *389*, 198–213.
[2] Chen, R.; Li, Q.; Yu, X.; Chen, L.; Li, H. *Chem. Rev.* **2020**, *120* (14), 6820–6877.
[3] Lu, Y.; Meng, X.; Alonso, J. A.; Fernández-Díaz, M. T.; Sun, C. *ACS Appl. Mater. Interfaces* **2019**, *11* (2), 2042–2049.
[4] Gao, L.; Song, M.; Zhao, R.; Han, S.; Zhu, J.; Xia, W.; Bian, J.; Wang, L.; Gao, S.; Wang, Y.; Zou, R.; Zhao, Y. *J. Energy Chem.* **2023**, *77*, 521–528.

Simple Access to a Series of Higher Substituted Pentafluoroorthotellurate-based Silanes and Germanes

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Among the few silicon compounds containing the pentafluoroorthotellurate group ($OTeF_5$, teflate) that have been reported, $Me_3SiOTeF_5$ is the only one that has been fully characterised.[1] In contrast, $Si(OTeF_5)_4$ was only briefly mentioned in the literature and its characterization is limited to its melting point.[2] Therefore, we investigated the substitution of chlorides in different organosilicon chlorides with teflate groups towards silicon compounds with an increasing teflate content.

Inspired by the synthesis of $Me_3SiOTeF_5$, several other $R_3SiOTeF_5$ (R = alkyl, aryl) compounds could be obtained by reacting $HOTeF_5$ or the easier to handle $AgOTeF_5$ and the corresponding R_3SiCl. Based on these results, synthetic routes for $R_2Si(OTeF_5)_2$ (R°=°Me, Et, ^{i}Pr, Ph) and $RSi(OTeF_5)_3$ (R = Me, Et, ^{t}Bu, Ph) species were developed. Currently we are adapting the synthesis to the corresponding germanes $R_xGe(OTeF_5)_{4-x}$ ($x = 3–0$, R = aryl, alkyl) and have already been able to make $Ph_3GeOTeF_5$, $Me_2Ge(OTeF_5)_2$ as well as $Ph_2Ge(OTeF_5)_2$ accessible. Moreover, the Lewis acidity of pentafluoroorthotellurate-based silanes and germanes $R_xE(OTeF_5)_{4-x}$ ($x = 3–0$, R = aryl, alkyl, E = Si, Ge) was investigated.

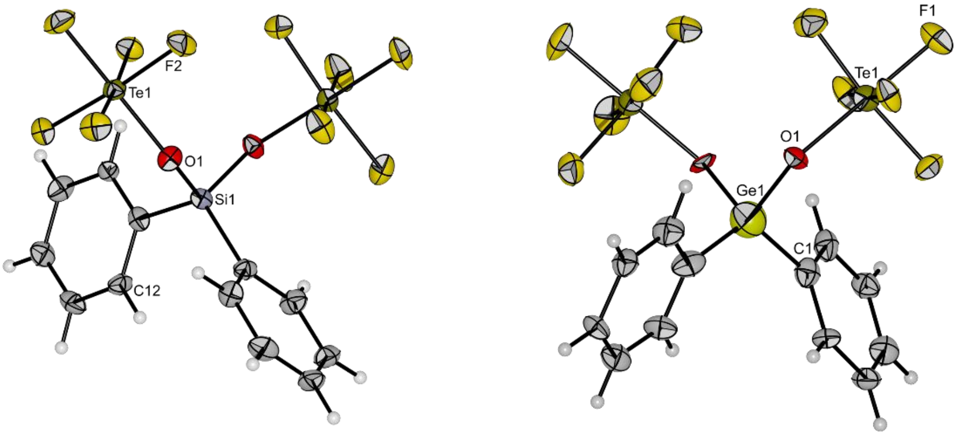

Figure 1. Molecular structure of $Ph_2Si(OTeF_5)_2$ and $Ph_2Ge(OTeF_5)_2$ in the solid state. Thermal ellipsoids are set at 50% probability.

References

[1] M. A. Ellwanger, C. von Randow, S. Steinhauer, Y. Zhou, A. Wiesner, H. Beckers, T. Braun, S. Riedel, *Chem. Commun.* **2018**, *54*, 9301-9304.

[2] F. Sladky, H. Kropshofer, *J. Chem. Soc., Chem. Comm.* **1973**, 600-601.

Synthesis and Reactivity of Zinc-Fluoride Coordination Complexes

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Zinc fluoride coordination complexes represent an under-explored compound class with only a few fully characterised examples in the literature.[1-4] Their synthesis often requires use of toxic reagents such as Me_3SnF, while their reactivity as fluorinating agents have not been researched extensively. The use of F-gases as a fluorine source for the synthesis of chemically upgraded fluorocarbons is an attractive process due to their prevalence in society and serious environmental impact. In this work, we report a series of zinc fluoride complexes synthesised by defluorination of a range of fluoride sources (pentafluorobenzonitrile, HFCs, HFOs) and subsequent coordination of 4-dimethylaminopyridine (DMAP). The structure and bonding of four isolated compounds has been investigated by NMR spectroscopy (^{1}H, ^{19}F, DOSY), X-ray crystallography and calculations (DFT, AIM). When compared to other molecular main group fluoride reagents,[5,6] preliminary studies show a good scope of reactivity towards electrophiles including silanes, benzoic anhydride, haloaryls and haloalkyls – likely due to relatively weak nature of Zn–F bonds. Computational studies, along with isolation of an intermediate in the reaction, have been used to probe the mechanism of the reaction.

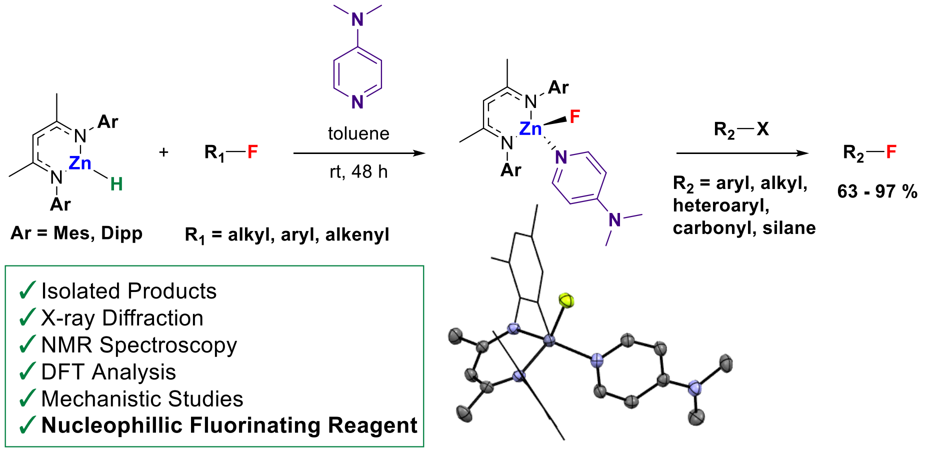

Figure 1. Overview of the synthesis of zinc fluoride complexes and subsequent reactivity for fluorination of electrophiles.

References

[1] W. Kläui, U. Schilde and M. Schmidt, *Inorg. Chem.* **1997**, *36*, 1598-1601.
[2] H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt and M. Noltemeyer, *Chem. Commun.* **2001**, *12*, 1118-1119.
[3] D. G. Shlian and G. Parkin, *Organometallics*, **2022**, *41*, 3435-3447.
[4] M. Rauch, Y. Rong, W. Sattler and G. Parkin, *Polyhedron*, **2016**, *103*, 135-140.
[5] D. J. Sheldon, J. M. Parr and M. R. Crimmin, *J. Am. Chem. Soc.* **2023**, *145*, 10486-10490.
[6] C. Patel, E. André-Joyaux, J. A. Leitch, X. Martínez de Irujo-Labalde, F. Ibba, J. Struijs, M. A. Ellwanger, R. Paton, D. L. Browne, G. Pupo, S. Aldridge, M. A. Hayward, V. Gouverneur, *Science*, **2023**, *381*, 302-306.

The Trifluorooxygenate Anion $[OF_3]^-$: Spectroscopic Evidence for a Binary, Hypervalent Oxygen Species

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Experimental evidence for hypervalent compounds of second-row elements is still scarce in literature.[1] The trifluorooxygenate anion $[OF_3]^-$ belongs to this class of compounds and has been predicted by several quantum chemical studies to be stable.[2] Some studies reported a D_{3h}-symmetric trigonal-planar structure to be the global minimum, which contradicts the VSEPR prediction. Since no experimental evidence of this compound has been reported so far, we isolated this compound under cryogenic conditions in a neon matrix by reacting OF_2 with free fluoride ions F^- generated by laser ablation of alkali metal fluorides MF (M = Li–Cs). IR spectroscopy confirms the C_{2v}-symmetric T-shape structure of $[OF_3]^-$ as predicted by the VSEPR model and calculations at the CCSD(T) level. $[OF_3]^-$ features one 2c-2e bond and one 3c-4e bond as shown by NLMO analysis, explaining the different bond lengths in the molecule. The ion pairs MOF_2 (M = Na–Cs) of the unknown $[OF_2]^{\bullet-}$ have also been detected in the experiments.[3]

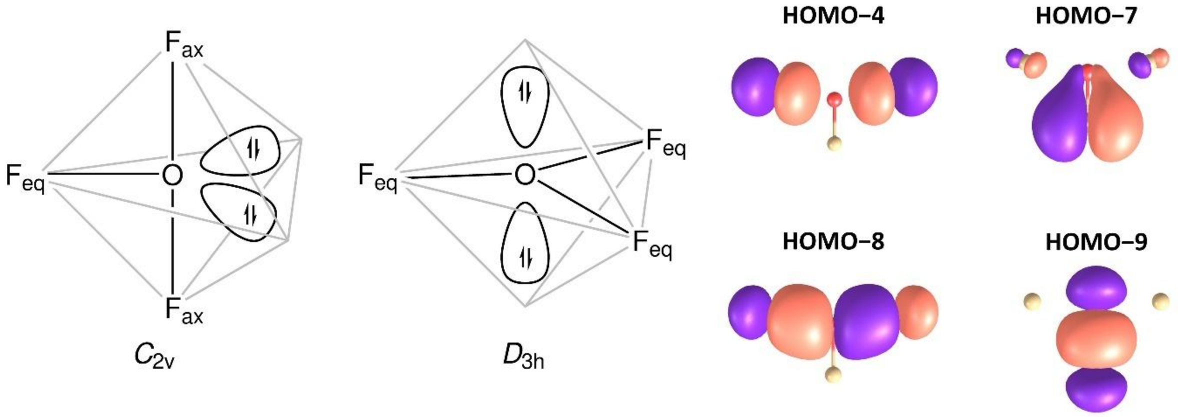

Figure 1. Left: Possible structural arrangements for $[OF_3]^-$. Right: NLMOs of $[OF_3]^-$.

References

[1] M. C. Durrant, *Chem. Sci.* **2015**, *6 (11)*, 6614-6623.

[2] a) V. P. Oliveira, E. Kraka, F. B. C. Machado, *Inorg. Chem.* **2019**, *58 (21)*, 14777-14789; b) I. Anusiewicz, S. Freza, C. Sikorska, P. Skurski, *Chem. Phys. Lett.* **2010**, *493 (4)*, 234-237; c) I. V. Getmanskii, R. M. Minyaev, V. I. Minkin, *Russ. Chem. Bull.* **2012**, *61 (11)*, 2036-2048; d) D. J. Grant, T.-H. Wang, M. Vasiliu, D. A. Dixon, K. O. Christe, *Inorg. Chem.* **2011**, *50 (5)*, 1914-1925.

[3] D. F. Meyer, R. Medel, S. Riedel, *Angew. Chem. Int. Ed.* **2024**, *63 (51)*, e202413758.

Electrochemical Fluorination – a Versatile Tool for the Large Scale Synthesis of Partially Fluorinated Building Blocks

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The incorporation of fluorine into molecules and materials typically results in unique properties that lead to applications in different fields, especially in pharmaceutics, agrochemicals, and energy-related materials [1]. The electrochemical fluorination (ECF) based on the Simons process is a highly efficient and reliable method for the synthesis of fluorinated building blocks [2]. Although the literature almost exclusively describes perfluorination of substrates, ECF turned out to be a valuable method for the preparation of partially fluorinated compounds, as exemplified by the synthesis of different partially fluorinated methyl- and ethyltriflates and -nonaflates. In contrast to well established methods, ECF offers the opportunity to straightforward perform large scale experiments of several hundred grams using inexpensive chemicals and electricity [3].

In the classical Simons process usually one or more hydrogen atoms are exchanged by fluorine and to the best of our knowledge, no investigation concerning isotope effects, *i.e.* electrochemical fluorination of deuterated starting materials has been performed. A significant isotope effect with regard to the fluorination rate was observed. Surprisingly, no hydrogen-deuterium exchange was observed during ECF in anhydrous hydrogen fluoride. In summary, an easy entry towards partially fluorinated compounds that contain either hydrogen or deuterium was developed [3].

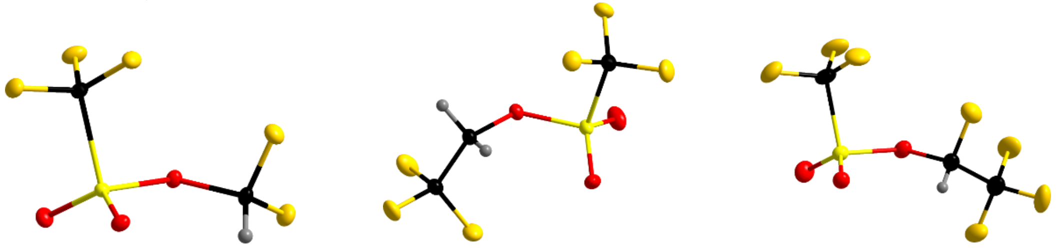

Figure 1. Solid state structure of $CF_3SO_2OCHF_2$, $CF_3SO_2OCH_2CF_3$ and $CF_3SO_2OCHFCF_3$.

References

[1] Kirsch, P. *Modern Fluoroorganic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2013**.
[2] Ignate'ev, N. V. *Electrochemical Fluorination: A Powerful Tool for the Preparation of Organofluorine Compounds* in *Modern Synthesis Processes and Reactivity of Fluorinated Compounds* (Eds.: H. Groult, F. Leroux, A. Tressaud), Elsevier Inc., **2017**, London, UK.
[3] T. Knuplez, L. N. Schneider, T. Preitschopf, Y. K. J. Bejaoui, L. Zapf, N. Schopper, K. A. M. Maibom, J. A. P. Sprenger, F. Gehrke, S. Lorenzen, R. Graf, R. Bertermann, I. Fischer, N. V. Ignat'ev, M. Finze, *Chem. Eur. J.* **2023**, 29, e202302701.

Nitrosyl Fluoride (FNO) and Nitryl Fluoride (FNO_2) as Fluorinating Agents for Inorganic Materials

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Nitrosyl fluoride FNO was discovered in 1905 separately in France by Henri Moissan [1] and in Germany by Otto Ruff [2]. Its synthesis, originally described by Moissan as a simple combination of nitrogen monoxide NO and fluorine F_2 in stoichiometric proportions, must however be carried out with caution, due to the extreme reactivity between the two species [3]. Other methods than combining the two compounds often lead to poor yields or extended periods of time in order to obtain nitrosyl fluoride [4]. Nitryl fluoride FNO_2 was first mentioned in 1905 by Moissan and Lebeau [5], but was fully described by Otto Ruff *et al.* in 1932 [6]. The synthesis is similar to that of nitrosyl fluoride, except that the latter is significantly less vigorous. The difficulty of having an installation using molecular fluorine F_2 and the behavior of the syntheses may explain the reasons why these two compounds were very little described in literature or used as fluorinating agents. This work will present the fluorination device which was entirely constructed from scratch and dedicated to the synthesis and the study of these two compounds. Their reactivity towards uranium hexafluoride (UF_6) will also be addressed.

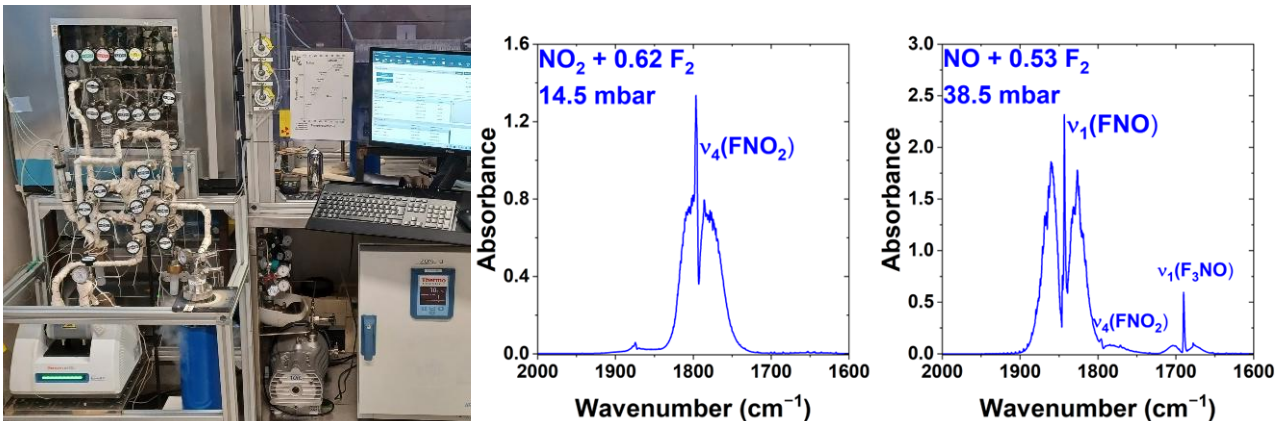

Figure 2: Picture of the experimental setup (Left), infrared spectrum of FNO_2 (Middle) and FNO (Right) in the 1600-2000cm^{-1} range

References

[1] H. Moissan, P. Lebeau, C. R. Des S. de l'Ac. Des Sci., **1905,** 140, 1573–1577.
[2] O. Ruff, K. Stäuber, Z. Für Anorg. Chem., **1905,** 47, 190–202.
[3] A.V. Faloon, W.B. Kenna, J. Am. Chem. Soc., **1951,** 73, 2937–2938.
[4] C.T. Ratcliffe, J.M. Shreeve, Chem. Comm., **1966,** 19, 674–675.
[5] H. Moissan, P. Lebeau, C. R. Des S. de l'Ac. Des Sci., **1905,** 140, 1621–1626.
[6] O. Ruff, W. Menzel, W. Neumann, Z. Für Anorg. Und Allg. Chem., **1932,** 208, 293–303

PARALLEL SESSION VII

Organic Chemistry

Aminophosphonates Bearing Fluorine Atoms as Inhibitors of Aminopeptidases – Synthesis and Properties

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Aminophosphonates are compounds showing pronounced and interesting biological activity (e.g. are potent drugs against osteoporosis). Especially, considering the acidity and a steric impact, fluorinated phosphonates are frequently used as the non-hydrolysable and stable mimics of naturally occurring phosphates. Among others, their inhibitory activity *versus* aminopeptidases is of great interest. The search for a new strategies of the synthesis of these compounds is a consequence of the previous studies in our group. Our research has been focused on new approach to a stereocontrolled synthesis of several mono and difluorinated aminophosphonates and later their dipeptides analogues.

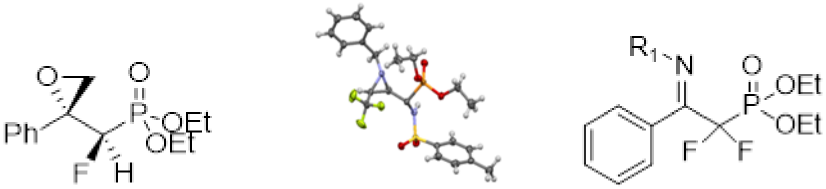

Figure 1. Examples of some intermediates used in the fluorophosphonates preparation

Novel Approaches in Asymmetric Catalytic Synthesis of Halo-organic Compounds

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Geminal dihaloalkanes (and the relative geminal difunctional compounds) constitute an attractive class of polyfunctional materials. However, the development of their chemistry has been an uneven process, most likely, due to the lack of practical and high yielding methods of their synthesis. We have established selective and efficient approach to the synthesis of non-activated germinal (*fluoro*)haloalkanes thanks to our recently developed methods for decarboxylative halogenation.

We will demonstrate a versatile employment of geminal dihaloalkanes and other difunctional compounds in asymmetric nickel-catalysed transformations. Thus, we will show an efficient approach to enantioselective construction of linear secondary *fluoro*alkanes, bearing an F-containing stereocenter at β, γ, δ and even ε-positions from the functional group, via stereoconvergent cross-coupling reactions [1]. An influence of fluoro- (or CF_3) substitution on stabilization of alkyl radical (a key intermediate in these reactions) will be discussed. We will demonstrate an implementation of such radicals in enantioselective catalytic synthesis of chiral α-trifluoromethyl benzhydrils, alcohols and ethers [2]. In addition, an employment of organotitanium materials as efficient nucleophilic partners in asymmetric cross-couplings will be revealed.

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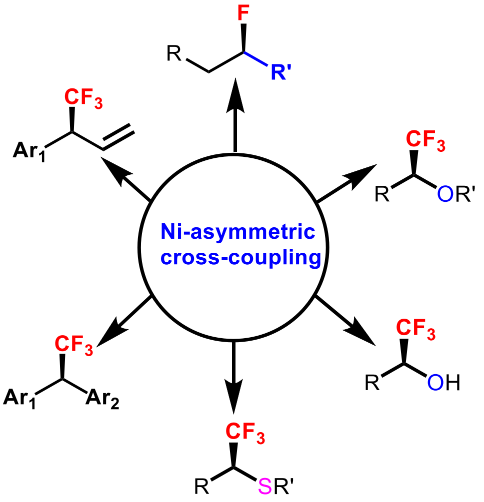

References

[1] *J. Am. Chem. Soc*. **2014**, *136*, 1305. (b) *J. Am. Chem. Soc.* **2015**, *137*, 2542. (c) *Chem. Sci.* **2016**, *7*, 2762

[2] *Nat. Commun*. **2018**, *9*, 3566. (b) *J. Am. Chem. Soc.* **2019**, *141*, 10994.

The Value of Fluorine in Agricultural Chemistry

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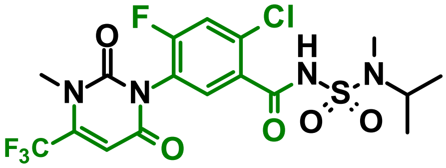
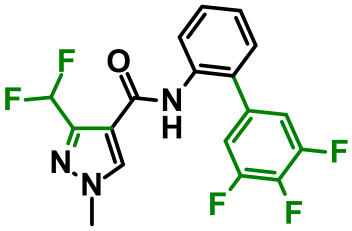
Inventing, developing, and commercializing new chemistry and products rapidly is a key for sustained profitability in the agrochemical, fine and specialty chemical, and pharmaceutical markets. New products will require the development of efficient synthetic routes and robust manufacturing processes.

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.



Kixor^R (H)



Xemium^R (F)

Effect of Amine Deprotonation on SuFEx: Synthesis of Sulfonamides

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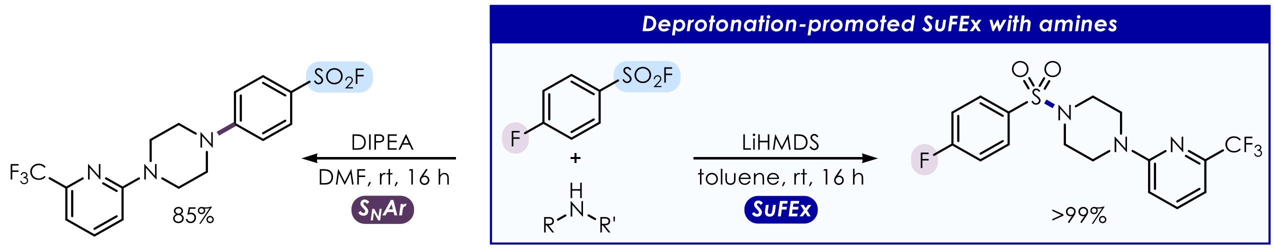
Sulfur Fluoride Exchange (SuFEx)[1] is a powerful click reaction and an efficient tool for making S-O, S-N and S-C connections.[2] Although well-explored, mechanistic aspects of this process remain a topic of discussion.[3] While SuFEx with O-nucleophiles typically proceeds rapidly, reactions with amines often appear to be more challenging. This difference may arise from the fact that O-nucleophiles react as anions (e.g., phenolates), whereas amines in their neutral form, therefore a different mechanism applies.[4] Our hypothesis is that amine deprotonation could accelerate the process and facilitate smooth fluoride substitution.
Herein, we report deprotonation-promoted SuFEx reaction of sulfonyl fluorides with amines. The process involves equilibrium deprotonation of amine using a lithium amide base, LiHMDS. A series of sulfonamides was synthesized in good to excellent yields, often without the need for column chromatography. For the model substrate 4-fluorobenzenesulfonyl fluoride, we observed S_NAr vs SuFEx selectivity. Neutral amines in DMF preferred aromatic substitution, whereas deprotonated ones reacted exclusively via SuFEx.[5]



This procedure is particularly beneficial for otherwise less nucleophilic aryl amines, as they are readily deprotonated under the reaction conditions, allowing their anionic form to react efficiently with the fluorosulfonyl center. Our findings contribute to a deeper understanding of the SuFEx mechanism, and the presented approach serves as an alternative to other strategies described in the literature, which utilize catalytic or stoichiometric promoters such as $Ca(NTf_2)_2$,[6] HOBt[7] and *N*-heterocyclic carbenes.[8]

References

[1] Dong, J.; Krasnova, L.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.*, **2014**, *53*, 9430–9448.
[2] Homer, J. A.; Xu, L.; Kayambu, N.; Zheng, Q.; Choi, E. J.; Kim, B. M.; Sharpless, K. B.; Zuilhof, H.; Dong, J.; Moses, J. E. *Nat. Rev. Methods Primers*, **2023**, *3*, 58.
[3] Barrow, A. S.; Smedley, C. J.; Zheng, Q.; Li, S.; Dong, J.; Moses, J. E. *Chem. Soc. Rev.*, **2019**, *48*, 4731–4758.
[4] Li, B.-Y.; Voets, L.; Van Lommel, R.; Hoppenbrouwers, F.; Alonso, M.; Verhelst, S. H. L.; De Borggraeve, W. M.; Demaerel, J. *Chem. Sci.*, **2022**, *13*, 2270–2279.
[5] Dudziński, J.; Bochra, J.; Barbasiewicz, M. *Synthesis*, **2024**, *Article in Press*, DOI: 10.1055/a-2446-7967.
[6] Mahapatra, S.; Woroch, C. P.; Butler, T. W.; Carneiro, S. N.; Kwan, S. C.; Khasnavis, S. R.; Gu, J.; Dutra, J. K.; Vetelino, B. C.; Bellenger, J.; am Ende, C. W.; Ball, N. D. *Org. Lett.*, **2020**, *22*, 4389–4394.
[7] Wei, M.; Liang, D.; Cao, X.; Luo, W.; Ma, G.; Liu, Z.; Li, L. *Angew. Chem. Int. Ed.*, **2021**, *60*, 7397–7404.
[8] Lin, M.; Luo, J.; Xie, Y.; Du, G.; Cai, Z.; Dai, B.; He, L. *ACS Catal.*, **2023**, *13*, 14503–14512.

An Unusual Reaction of Fluorine Substitution in Pentafluoroiodo- and Pentafluorobromobenzenes by Amino Species Running at Ambient Conditions

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A series of the amine - halogen bond donor system (amine = ethylenediamine, phenantroline, pyrrolidine, hexamethylenediamine, hexamethylenetetramine, quinoline; XB donor = pentafluoroiodobenzene, pentafluorobromobenzene, tetrafluorodiiodobenzene) was investigated by the means of refractometry and F^{19} NMR. In addition to the formation of the expected halogen-bonded complexes, an unusual reaction of fluorine substitution on amine species running at ambient conditions was observed in some cases. All products were characterized by NMR, Raman spectroscopy and single crystal X-ray diffraction. The results obtained by various methods and of the formation of definite products are in very good agreement.

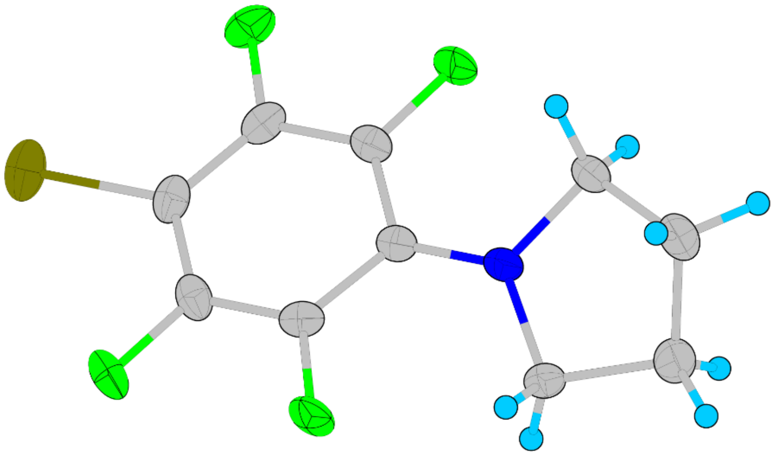

Figure 1. An adduct of pentafluorobromobenzene and pyrrolidine obtained by click-reaction at ambient conditions.

Cross-coupling Reactions Using Multihalogenated Alkenes Synthesized from Halothane

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The synthesis methods of fluoroalkenes have been reported, because fluoroalkenes are utilized in the industrial fields such as medicines, agrochemicals, polymers and liquid crystals. For example, one of the methods is using fluoroalkanes as fluorine-containing building blocks under basic conditions.[1, 2] Recently, we succeeded in synthesizing multihalogenated alkenes (**1** or **1’**) from the reactions between nucleophiles such as phenols or indoles and 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane).[3] **1** or **1’** has bromine, chlorine and fluorine atoms, especially bromine atom is reactive and useful to transform **1** or **1’** to new fluoroalkenes. Therefore, we challenged Suzuki—Miyaura or Sonogashira cross-coupling reactions with **1** or **1’** to gain various fluoroalkenes (**3** or **3’**).[4]

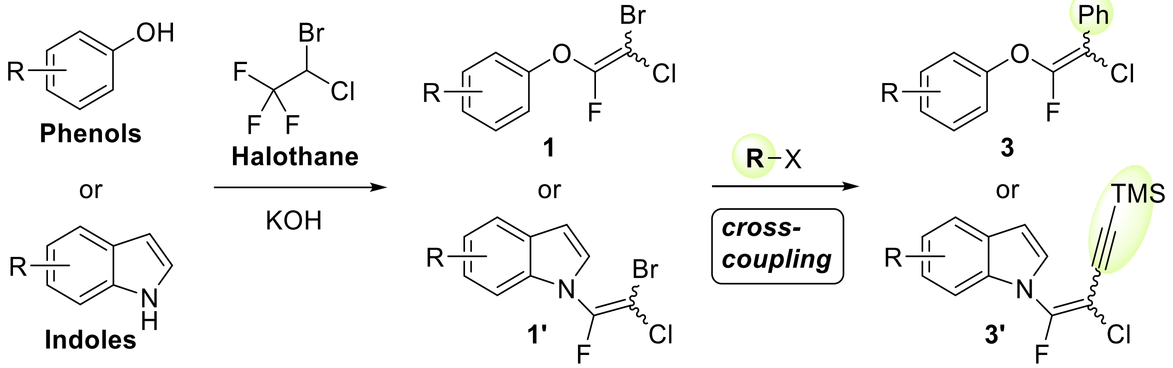

Figure 1. Synthesis methods of fluoroalkenes using halothane

References
[1] Wu, K.; Chen, Q.-Y.; *Tetrahedron*, **2002**, *58*, 4077-4084
[2] Tang, X.-J.; Chen, Q.-Y.; *Synlett*, **2020**, *31*, 2046-2048
[3] Karuo, Y.; Tarui, A.; Sato, K.; Kawai, K.; Omote, M. *Beilstein J. Org. Chem.*, **2022**, *18*, 1567–1574
[4] Karuo, Y.; Tarui, A.; Sato, K.; Kawai, K.; Omote, M. *Beilstein J. Org. Chem.*, **2024**, *20*, 2691–2703

Defluorinative Synthesis of Monofluoroalkenes via Photoredox C–C Coupling of α-Aminoalkyl Radicals and Allylic Difluorides

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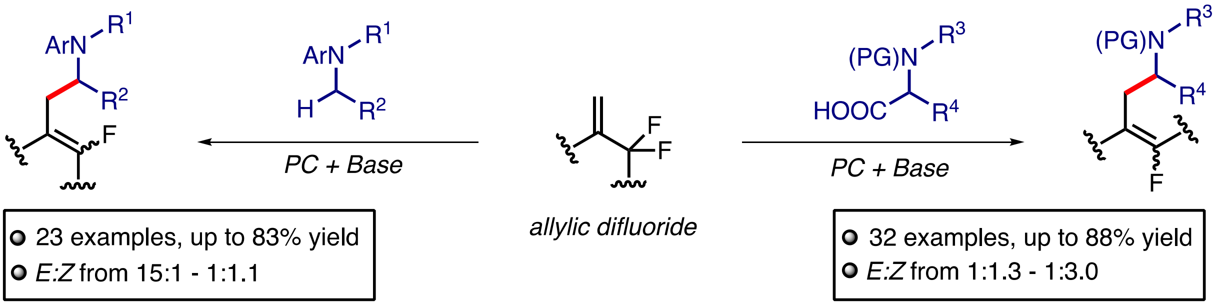
Monofluoroalkenes are of pharmaceutical interest due to emulating the biological properties of peptide bonds. With an absence of these functional groups existing in nature, the introduction of monofluoroalkenes onto biologically relevant molecules is an active research area. Among others, these motifs can be accessed through selective C–F bond activation of allylic difluorides, however this process is difficult as the C–F bond is essentially inert. Despite this challenge, we have developed a radical-based approach to the above transformation via the photocatalytic formation of α-aminoalkyl radicals from *N*-alkylanilines. This reaction proceeds through regioselective radical addition across allylic difluorides, followed by SET and a fluoride elimination event to yield monofluoroalkenes. Furthermore, we diversified into using Boc-protected amino acids as radical precursors, which can also generate α-aminoalkyl radicals under photocatalytic conditions. This requires a reversal of both initial steps in the mechanism: deprotonation of the carboxylic acid moiety must precede the photocatalytic oxidation step, followed by decarboxylation.

Both processes have been fully optimized and show good to excellent yields with over 50 combined examples. Reactivity trends have been discovered based on the nature of the radical precursor and allylic difluoride. In order to unlock full reactivity, the reaction conditions have been fine-tuned for different substrates, including the use of different photocatalysts. When the reaction is performed using acyclic allylic difluorides, the ratio of *E* and *Z* products vary significantly based on steric influences at the pre-elimination intermediate. Postfunctionalization of the monofluoroalkene-containing products has been performed, which highlights potential for further transformations into relevant molecules, such as peptide mimics for drug design in pharmaceutical industries.



Scheme 1. C–C Coupling of photoredox-generated α-aminoalkyl radicals and allylic difluorides.

References

[1] Semeniuk, T.; Dudas, T.; Okeh, E.; Felesky, T.; Hamel, J.-D. *J. Org. Chem.* **2024,** *89*, 13669–13677.

PARALLEL SESSION VII

Organic Chemistry

Perfluoro-*tert*-Buty Anion: Preparation, Structure, and Reactivity

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As a "fat" analogue of the well-known trifluoromethyl anion (CF_3^-) , perfluoro-*tert*-butyl anion [$(CF_3)_3C^-$] has been largely neglected during the past 30 years, arguably owing to the challenge related to its preparation (requiring highly toxic precursors). Although this anion has been noted in literature, its X-ray single crystal structure still stays illusive. In this presentation, we wish to disclose the preparation of stable perfluoro-*tert*-butyl anion [$(CF_3)_3C^-$] and its X-ray single crystal structure. Furthermore, the unique reactivity and its synthetic potency of this perfluorinated carbanion will be also presented, together with the unique applications of various perfluoro-*tert*-butylated products.

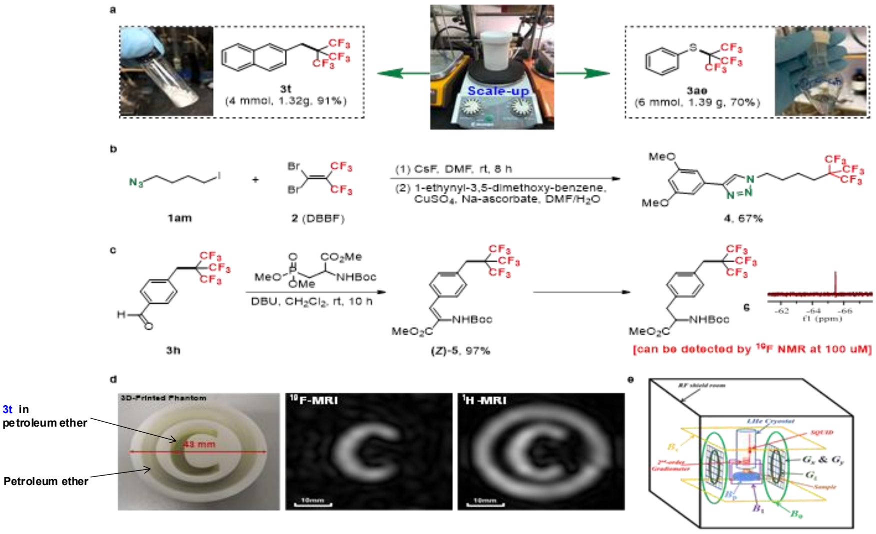

Figure 1. Perfluoro-*tert*-butylation and its applications.

References

[1] Wang, Q.; Tao, Q.; Dong, H.; Ni, C.; Xie, X.; Hu, J. *Angew. Chem. Int. Ed.* **2021**, *60*, 27318-27323.

[2] Wei, Z.; Wen, L.; Zhu, K.; Wang, Q.; Zhao, Y.; Hu, J. *J. Am. Chem. Soc.* **2022**, *144*, 22281-22288.

On the importance of Michaelis–Menten kinetics

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Michaelis–Menten kinetics usually refers to enzyme-catalysed chemical reactions. This study extends the validity of Michaelis–Menten kinetics into inorganic chemistry. It describes dry chemical etching of silicon induced by the molecular fluorine. The Michaelis–Menten equation is derived mathematically using the chemical kinetics theory. It is well known that the Michaelis–Menten saturation curve is the section of the right rectangular hyperbola [1]. This fact is proved by a single mathematical operation. At a pressure lower than the Michaelis constant, highly precise measurements of the etching rate are needed because the formation of SiF_2 molecules is the etching rate-limiting process. While at a pressure higher than the Michaelis constant, the desorption of the reaction product becomes the etching rate-limiting process, and high-purity reactants must be used to avoid the passivation of the silicon surface. The Michaelis constant is defined as the ratio of rate constants. As a result, the Michaelis constant becomes temperature dependent in the cases where the activation energies of these rate constants significantly differ.

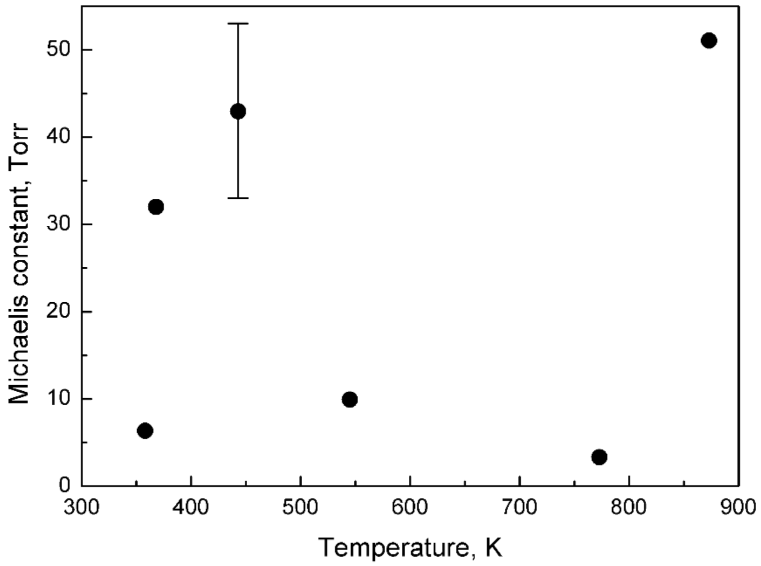

Figure 1. The dependence of the Michaelis constant on the temperature obtained by fitting the experimental data.

Reference

[1] Michaelis–Menten kinetics during dry etching processes, Knizikevičius, R. PLoS One, 2024, 19, e0299039.

From Trifluoromethoxylation to Difluorophosgene Chemistry: A Journey with 2,4-Dinitro-trifluoromethoxybenzene (DNTFB)

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Due to their specific properties, fluorinated compounds are used in a wide range of applications, from life sciences to materials. These last years, there has been a growing interest in the search for new emerging fluorinated groups with specific properties.

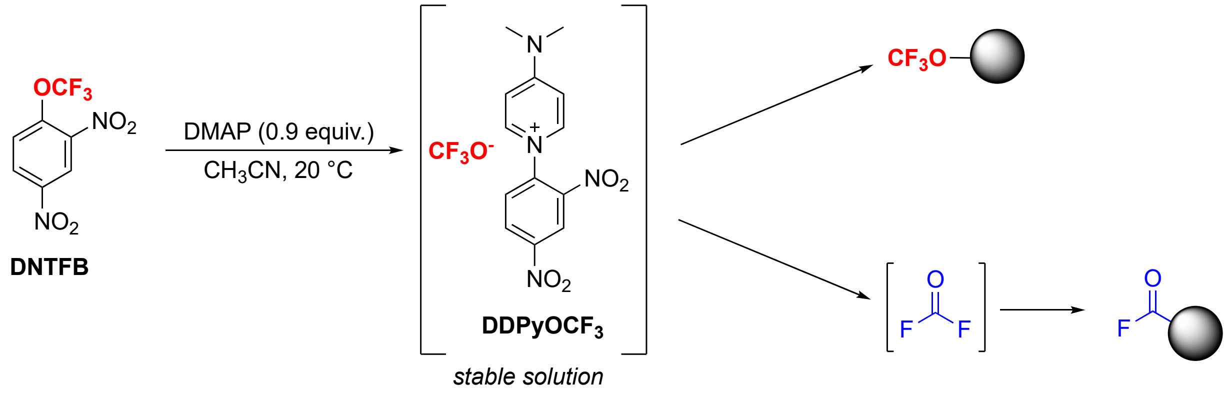
Such interest requires the development of new efficient reagents for the easy synthesis of different substrates bearing these substituents.

In this context, 2,4-dinitro-trifluoromethoxybenzene (DNTFB) represents a cheap, easy to handle and promising reagent. The stable salt DDPyOCF$_3$ can be easily obtained from this compound.

This salt can be used to perform nucleophilic trifluoromethoxylation reaction to easily access to CF$_3$O-molecules.

Trifluoromethoxyde anion (CF$_3$O$^-$) is also able to easily generate difluorophosgene which can be the engaged in various reaction to obtain new families of fluorinated compounds.

First studies on the reactivity and the use of DNTFB in the synthesis of molecules bearing various fluorinated groups will be described.[1]



Scheme 1. Formation and reactivity of DDPyOCF$_3$ from DNTFB.

References

[1] a) C. Bonnefoy, E. Chefdeville, A. Panossian, G. Hanquet, F. R. Leroux, F. Toulgoat, T. Billard, *Chem. Eur. J.* **2021**, *27*, 15986-15991; b) C. Bonnefoy, E. Chefdeville, C. Tourvieille, A. Panossian, G. Hanquet, F. Leroux, F. Toulgoat, T. Billard, *Chem. Eur. J.* **2022**, *28*, e202201589; c) C. Bonnefoy, A. Panossian, G. Hanquet, F. R. Leroux, F. Toulgoat, T. Billard, *Chem. Eur. J.* **2023**, *29*, e202301513; d) C. Bonnefoy, A. Gallego, C. Delobel, B. Raynal, M. Decourt, E. Chefdeville, G. Hanquet, A. Panossian, F. R. Leroux, F. Toulgoat, T. Billard, *Eur. J. Org. Chem.* **2024**, *27*, e202400142; e) L. Wisson, G. Hanquet, F. Toulgoat, T. Billard, A. Panossian, F. R. Leroux, *Eur. J. Org. Chem.* **2024**, *27*, e202400388.

Lewis Acid-Catalyzed Carbofluorination via Fluoride Recycling

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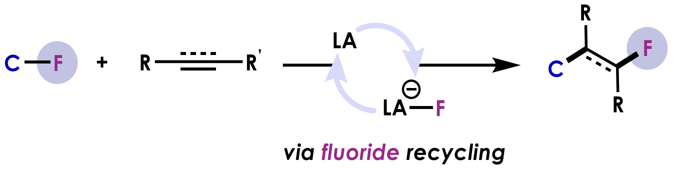
My research program focuses on the synthesis, reactivity, and application of novel fluorine-containing building blocks in organic chemistry. The Le Lab is driven by two primary objectives: (1) developing simple, practical protocols for the preparation of fluorinated building blocks, and (2) harnessing their unique fluoride-enabled reactivity to advance synthetic methodology. Vinyl and alkyl fluorides occupy a privileged space in medicinal chemistry programs, as the presence of a C–F bond can greatly modulate the pharmacological properties of a small molecule. Over the past few years, my group has focused on the application of fluorinated electrophiles in complexity-building transformations that recycle the valuable fluorine atom.[1] This seminar will showcase the development of Lewis acid-catalyzed carbofluorination reactions, which involve the formation of a new C–C and C–F bond across a π-system, using carbamoyl or acyl fluorides as the C–F bond donor.[2,3] In addition to being fully atom-economical, such methods eliminate the need for external fluorinating reagents, which are often costly and pose specific safety challenges. Mechanistic studies involving reaction kinetics, Hammett studies, and DFT calculations will be presented to elucidate a common reaction pathway involving "fluoride recycling," which is governed by the precise balance of catalyst fluorophilicity.



Scheme 1. Lewis Acid-Catalyzed Carbofluorination Reaction

References

[1] McKnight, E. A.; Cadwallader, D.; Le, C. M. *Eur. J. Org. Chem.* **2024**, *27*, ejoc.202300017.

[2] McKnight, E. A.; Arora, R.; Pradhan, E.; Fujisato, Y.; Ajayi, A.; Lautens, M.; Zeng, T.; Le, C. M. *J. Am. Chem. Soc.* **2023**, *145*, 11012–11018.

[3] McKnight, E. A.; Fujisato, Y. J.; Khanal, N.; Le, C. M. *Org. Lett.* **2025**, ASAP, 10.1021/acs.orglett.5c00154.

Reactions of Hexafluorothioacetone Dimer (HFTAD) with Terpenes

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The utilization of hexafluorothioacetone dimer (HFTAD) as a precursor to monomeric $(CF_3)_2C{=}S$ (hexafluorothioacetone, HFTA) has been well-established at this point. Recent studies have elucidated the diverse reaction pathways of HFTA with organic substrates, including [2+2], [2+4] cycloadditions, and ene-reactions. However, the majority of reported reactions have employed substrates capable of engaging only a single reaction type, resulting in a lack of comprehensive information on the relative preferences of different type of reaction in scientific literature.

Terpenes are considered "ideal" substrates for investigating this type of chemical transformation due to their chemical diversity and availability. The present study aims to present the outcomes of reactions (performed in the absence of metal fluoride catalyst) involving various types of terpenes with HFTAD. Furthermore, the observed trends in the chemical behaviour of terpenes in these reactions will be analysed.

HF Shuttling for the Chemical Recycling of Fluorocarbons

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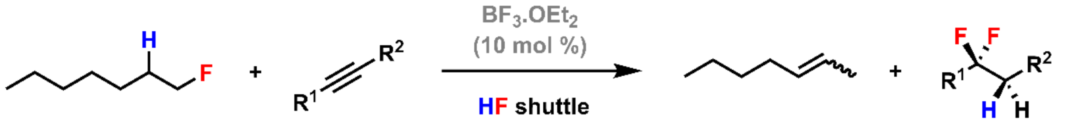
Fluorocarbons are essential to our way of life, with uses ranging from materials and refrigerants to pharmaceuticals and agrochemicals. However, fluorocarbons are overwhelmingly treated as “single-use”, with little to no recycling. Disposal routes face increasing scrutiny due to emerging research on the pervasiveness of per- and poly- fluorinated substances and the impact of exposure on human health.[1,2] Methodologies for recycling fluorocarbons are therefore highly attractive.

Hydrofluorination is an essential methodology for the synthesis of fluorocarbons, but typically requires toxic and difficult to handle reagents, such as hydrofluoric acid, Py.HF, Et_3N.HF and DBU.HF, and can suffer from poor selectivity and reactivity.[3] There are few methodologies which achieve both hydrofluorination and dehydrofluorination in a single reaction sequence.

In this work, we report BF_3.OEt_2 as a catalyst for shuttling equivalents of HF from fluoroalkanes to alkynes and acid anhydrides, generating difluoroalkanes and acyl fluorides respectively.[4] Numerous potentially sensitive functional groups including halogens, protected amines, esters and thiophenes are tolerated. Density functional theory calculations have been used to probe the mechanism of the reaction. The system has been leveraged for the dehydrofluorination of both commercial and post-consumer poly(vinylidene difluoride) (PVDF) materials, the second most used fluoropolymer worldwide. Characterisation including IR, XPS, XRD and elemental analysis of the polymer products indicate a high degree of dehydrofluorination, demonstrating HF shuttling’s value as a proof-of-concept recycling methodology.[5]



21 examples (36-78 %)
tolerates CL, Br, I, CF_3, ester, thienyl
PVDF as an HF donor

Scheme 1. Overview of Lewis acid catalysed HF shuttle between fluoroheptane and alkynes.

References
1. H. Brunn, G. Arnold, W. Körner, G. Rippen, K. G. Steinhäuser, I. Valetin, *Environ. Sci. Euro.*, **2023**, *35*, 20
2. Z. Wang, H. C. DeWitt, C. P. Higgins, I. T. Cousins, *Environ. Sci. Technol.*, **2017**, *51*, 2508-2518
3. X. Bertrand, L. Chabaud, J. F. Paquin, *Chem. Asian J.*, **2021**, *16*, 563-574
4. S. E. S. Farley, D. Mulryan, F. Rekhroukh, A. Phanopolous, M. R. Crimmin, *Angew. Chem. Int. Ed.*, **2024**, *63*, e202317550
5. C. Heinekamp, A. G. Buzanich, M. Ahrens, T. Braun, *Chem. Commun.*, **2023**, *59*, 11224-11227

FLASH PRESENTATIONS

Activation of Perfluoro(methyl vinyl ether) at Rh(I) Phosphine Complexes: Metal-Centered versus Phosphine Mediated Decarbonylation

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This study investigates the reactivity of perfluoro(methyl vinyl ether) [PMVE, CF_2=CF(OCF_3)] towards rhodium(I) phosphine complexes, focusing on the C-F and C-O bond activation mechanisms and decarbonylation processes. Using the complex [Rh(H)(PEt_3)$_3$], we observed unprecedented reactivity pathways that are distinguish from previously studied fluoroolefins.[1-4] Notably, in addition the coordination of PMVE to the Rh-centre at [Rh(H)(PEt_3)$_3$] and insertion of it into the Rh-H bond, the intermediate [Rh($CF_2CFHOCF_3$)(PEt_3)$_3$] undergoes *β*-OCF_3 elimination. Furthermore, PMVE can insert into the Rh-F bond in *trans*-[Rh(F)(CO)(PEt_3)$_2$] leading to the formation of the *trans*-[Rh(CO)(CF(OCF_3)CF_3)(PEt_3)$_2$]. These reaction pathways offer a new route for metal-centered mediated decarbonylation at room temperature and open a new door for possible installation of the -CF(OCF_3)CF_3 group into organic molecules. Remarkably, this study highlights PMVE as an effective CO source, which is released not only through interaction with rhodium but also via a metal-free, phosphine-mediated process promoting the decarbonylation reaction. The latter is assessed by oxidative addition of PMVE at triethylphosphine to form fluorophosphoranes, (OCF_3)CF=CF($PFEt_3$), which subsequently release carbon monoxide gas upon decomposition.

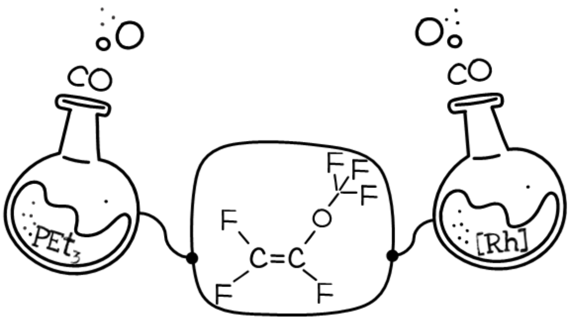

Figure 1. Schematic illustrating the CO production upon the reactivity of PMVE towards rhodium complexes and phosphine.

References

[1] Talavera, M.; Mollasalehi, S.; Braun, T. *Chem. Sci.* **2024**, *15*, 8472-8477.
[2] Talavera, M.; Braun, T. *Chem. Sci.* **2022**, *13*, 1130-1135.
[3] Talavera, M.; Braun, T. *Chem. Eur. J.* **2021**, *27*, 11926-11934.
[4] Talavera, M.; Braun, T. *Synlett* **2020**, *31*, 1760-1774.

C–F Bond Activation of Fluoroalkanes *via* Germylium Ions Catalysis

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In the last decades, metal-free C–F bond activation with main group compounds have gained attention, and compounds showing a strong Lewis-acidity are of particular interest.[1,2] Group 14 compounds are known to be good Lewis-acids and the Braun group started to explore the properties and reactivity of germylium systems towards C–F[3] and C=C[4] bonds.

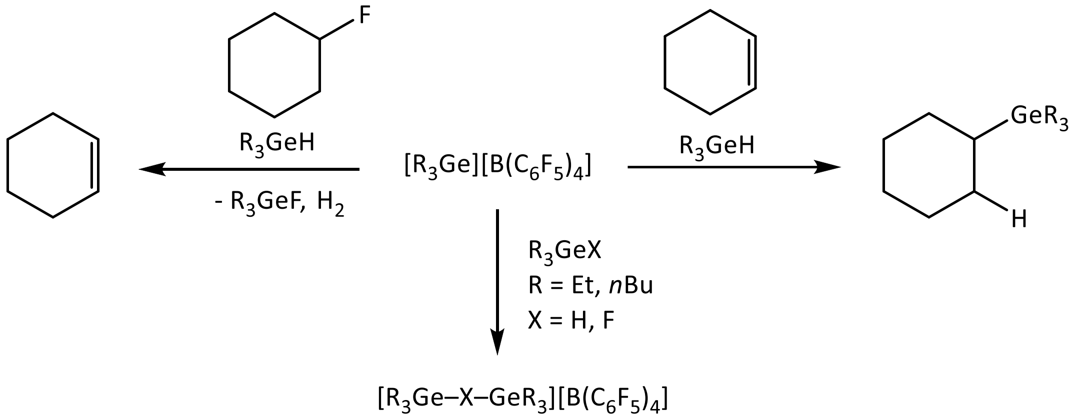

Figure 1. Reactivity of germylium ions with fluorocyclohexane, cyclohexene and other germane species.

Germylium ions $[R_3Ge][B(C_6F_5)_4]$ stabilized by a weakly coordinating anion could be isolated and reacted to further cationic derivatives (see **Figure 1.**). Their properties and reactivity were investigated and the germylium ions/germane system revealed an interesting reactivity towards the C–F bond activation of mono- and polyfluoroalkanes leading to the formation of dehydrofluorinated products, whereas reactions using *in situ* generated or isolated silylium ions exclusively lead to hydrodefluorinated products.[5,6] Moreover hydrogermylation of alkenes and alkynes using this same system has also been observed, opening up a new range of possibilities for the functionalisation of these substrates.

References

[1] Stahl, T.; Klare, H. F. T.; Oestereich, M. *ASC Catal.*, **2013**, 3, 1578−1587.
[2] Pei, R.; Chang, W.; He, L.; Wang, T.; Zhao, Y.; Liang, Y.; Wang, X. *Nat. Commun.,* **2024**, 15, 7943.
[3] Talavera, M.; Meißner, G.; Rachor, S.; Braun, T. *Chem. Comm.,* **2020**, 56, 4452–4455.
[4] Meißner, G.; Kretschmar, K.; Braun, T. *Angew. Chem. Int. Ed.,* **2017**, 56, 16338 –16341.
[5] Scott, V. J.; Celenligil-Cetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.*, **2005**, 127, 2852–2853.
[6] Douvris, C.; Stoyanov, E. S.; Tham, F. S.; Reed, C. A. *Chem. Comm.,* **2007**, 1145–1147.

Respirometric Analysis for Monitoring the Microbial Activity during Exposure to Perfluorobutanesulfonic and Perfluorohexanesulfonic Acid

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Microbial degradation of per- and polyfluorinated alkyl substances (PFAS) is an emerging area of research for mitigating environmental contamination [1]. While traditional chemical or physical methods struggle to break down these highly stable compounds, certain microorganisms have shown potential in degrading PFAS under specific conditions. These microbes utilize enzymes that can attack the C-F bonds and transform PFAS into less harmful substances. However, the biodegradation process is often slow, and more research is needed to identify efficient microbial strains and optimize environmental conditions [2]. The development of effective bioremediation techniques for PFAS could offer an eco-friendly solution for contamination management [3]. During our study, we conducted an experiment on the transformation of perfluorobutanesulfonic acid (PFBS) and perfluorohexanesulfonic acid (PFHxS) as model substances. In this study, the degradation of PFBS and PFHxS was monitored using a Micro-Oxymax Respirometer (Columbus Instruments, USA). The respirometer is a device that measures the production and consumption of various gases simultaneously. It operates in a 'Closed Loop Measurement Method' mode and measures changes in oxygen consumption and carbon dioxide production during microbial degradation. The microorganisms used were *Pseudomonas* isolated from PFAS-contaminated sites and under a PFAS selection pressure. They were inoculated in three different media: mineral with yeast extract (control), mineral with yeast extract and 5 ppm of PFBS, and mineral with yeast extract and 5 ppm of PFHxS.

Results suggest that all tested strains were active during exposure to PFBS and PFHxS, however one strain of *Pseudomonas* was slightly inhibited by the pollutants, whereas two other tested strains exhibited higher activity in the presence of these compounds compared to the control sample without PFAS. To further analyse the metabolic process involved, concentration of PFBS and PFHxS was monitored, as well as their transformation products.

Acknowledgement

This work was supported by the European Union's Horizon Europe Framework Programme, Twinning Western Balkans, under grant agreement No. 101059534 (PFAStwin).

References

[1] Berhanu, A., Mutanda, I., Taolin, J., Qaria, M. A., Yang, B., Zhu, D., *Sci. Total Environ.*, **2023**, 589, 160010.
[2] Kumar, R., Dada, T. K., Whelan, A., Cannon, P., Sheehan, M., Reeves, L., Antunes, E., *J. Hazard. Mater.*, **2023**, 452, 131212.
[3] Zhang, Z., Sarkar, D., Biswas, J. K., Datta, R., *Bioresour. Technol.*, **2022,** 344, 126223.

Novel Hexafluorosulfur Activation utilizing an Organic Photoredox Catalyst

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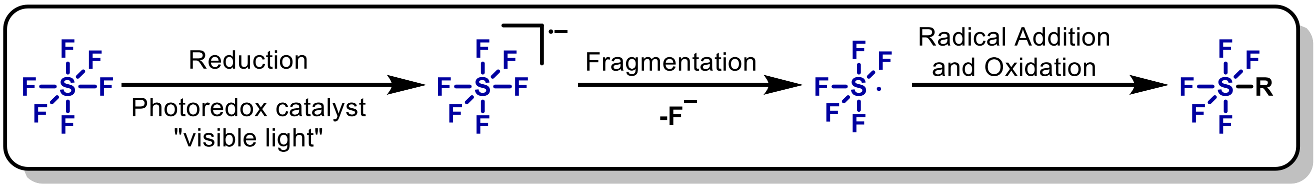
Pentafluorosulfanyl substituted compounds showcase a unique and novel utility in modern fluorine chemistry. In recent years the environmental issues of compounds employing fluorocarbon bonds have been becoming more apparent.[1] Therefore, the search for moieties with similar properties and their respective chemical transformation is essential. The pentafluorosulfanyl group is a prime candidate for such an area of application due to its unique electronic structure and steric demand.[2] Conclusively, we present the generation of high value chemicals bearing the pentafluorosulfanyl group, by reducing the inert and non-toxic sulfur hexafluoride via photoredox catalysis employing visible light.[3,4]



Scheme 1. General proposed mechanism of the photocatalytic reductive activation and addition of sulfur hexafluoride to yield a variety of high value pentafluorosulfanyl structures.

References

[1] M. Bonato; F. Corrà; M. Bellio; L. Guidolin; L. Tallandini; P. Irato; G. Santovito *Int. J. Environ. Res. Public Health*, **2020**, *17* (*21*), 8020.

[2] R. Kordnezhadian; B. Li, A. Zogu; J. Demaerel; W. M. De Borggraeve; E. Ismalaj *Chem. Eur. J.,* **2022**, *28*, e202201491.

[3] D. Rombach; H. Wagenknecht *ChemCatChem,* **2018**, *10*, 2955 – 2961.

[4] D. Rombach; H. Wagenknecht *Angew. Chem. Int. Ed.,* **2020**, *59*, 300 –303.

Investigating the Site-Specific Impact of Fluorine Substitution on Aromatic Interactions in a Tryptophan Zipper Peptide

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Fluorinated analogues of tryptophan (Trp) have found broad application as biocompatible NMR probes given fluorine's high sensitivity, broad chemical shift range, and its absence from biological systems[1,2]. While fluorine only minimally perturbs the molecular geometry of the Trp side chain, global implications are difficult to predict as they are highly regiospecific especially upon substitution of multiple Trp residues across a whole biological organism.[3,4] Herein we present a systematic study of the effect of fluoro-Trp substitution on the pairwise *edge-to-face* π-stacking interaction in the 12-residue β-hairpin peptide Trpzip2.[5] We employed a library approach to assess the regiospecific impact of all monofluorinated Trp derivatives on peptide structure and stability using circular dichroism (CD) and NMR. Global hairpin stability was improved or compromised upon site-selective incorporation of a single monofluoro-Trp regioisomer. Fluorine substitution revealed key CH/π contributions within the Trp/Trp packing, which could be fine-tuned based on the aryl-fluorine substitution pattern.

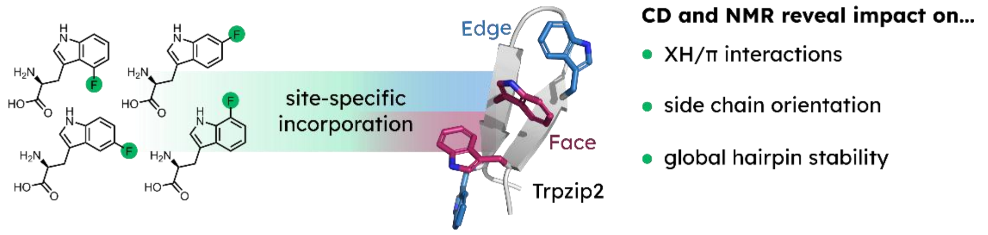

Figure 1. Graphical abstract. Analogues of the β-hairpin peptide Trpzip2 containing monofluoro-Trp regioisomers were chemically synthesized and studied by CD and NMR to evaluate the impact of fluorine-substitution on the *edge-to-face* Trp/Trp interaction.

References

[1] H. Qianzhu, E. H. Abdelkader, G. Otting, T. Huber, *J. Am. Chem. Soc.* **2024**, *146*, 19, 13641–13650.
[2] H. Welte, T. Zhou, X. Mihajlenko, O. Mayans, M. Kovermann, *Sci. Rep.* **2020**, *10*, 2640.
[3] F. Agostini, L. Sinn, D. Petras, C. J. Schipp, V. Kubyshkin, ..., B. Koksch, *ACS Cent. Sci.* **2021**, *7*, 81–92.
[4] C. Treiber-Kleinke, A. A. Berger, L. Adrian, N. Budisa, B. Koksch, *Front. Synth. Biol.* **2024**, *1*, 1345634.
[5] A. G. Cochran, N. J. Skelton, M. A. Starovasnik, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 5578–5583.

Development and Characterization of Innovative Materials for Photocatalytic Degradation of Perfluorooctanoic Acid

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Perfluorooctanoic acid (PFOA), a widely used member of per- and polyfluorinated alkyl substances (PFAS) in products like food packaging and non-stick cookware, has been released in the past into the environment in significant amounts and now due to this can be easily found in wastewater. Its stability, due to strong C-F bonds, makes it resistant to degradation [1]. PFOA and other PFAS have been classified as persistent organic pollutants (POPs) due to their harmful effects on human health and the environment [2]. Various methods, including photocatalysis, are being studied to remove PFOA from contaminated water. Photocatalysis shows promise as an effective, eco-friendly solution for PFOA degradation [3].

In this study we developed and characterized different photocatalysts to be used for the degradation of PFAS. We used photocatalysts based on aluminium oxide and zinc oxide, titanium oxide with tungsten oxide and titanium oxide with graphene oxide. The photocatalysts were prepared using the same method, plasma electrolytic oxidation (PEO), which immobilizes photocatalytic compounds on metal substrates such as titanium. This technique, which involves oxidation in an alkaline electrolyte, allows the oxide layer to be easily doped with various components, improving stability and recycling potential. The characterization of the photocatalytic coatings was carried out using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS). To confirm their efficacy, photocatalytic degradation of PFOA in an aqueous solution. Analysis by liquid chromatography and mass spectrometry confirmed that all photocatalysts are effective in PFOA degradation, while titanium oxide with tungsten oxide stood out, removing more than 90% of PFOA within 8 hours, which is expected and in accordance with the structures of the materials that we gained insight into after their detailed characterization.

Acknowledgement:

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References

[1] Zango, Z. U., Khoo, K. S., Garba, A., Kadir, H. A., Usman, F., Zango, M.U., Oh, W. D., Lim, J. W., *Environ. Res.,* **2023,** 221, 115326.

[2] Li, K., Gao, P., Xiang, P., Zhang, X., Cui, X., Ma, L.Q, *Environ. Int.,* **2017,** 99 43-54.

[3] Liu, J., Guo, C., Wu, N., Li, C., Qu, R., Wang, Z., Jin, R., Qiao, Y., He, Z., Feng, X., Zhang, Y., Wang, A., Gao, J., *Chem. Eng.*, **2022,** 435, 134627.

Search for Novel Superconductors in a Chemical Capacitor Setup

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The discovery of high-temperature superconductors (HTS) in 1986 initiated an enduring pursuit of novel superconducting materials, a research avenue that continues to attract scientists to this day. To achieve superconductivity, parent insulating compounds must be doped with a suitable amount of either electrons or holes. However, many compounds resist any doping attempts. To bypass these difficulties, a "chemical capacitor"[1][2] was designed to simultaneously control charge distribution and induce metallization in diverse compounds[3]. This method leverages the interaction between carefully selected oxidizing and reducing nanolayers, with a separator that modulates the interaction strength by varying its thickness and dielectric constant. In our study, we investigated fluorine compounds as wide gap insulators in the chemical capacitor setup, specifically CaF_2, $CsPbF_3$, KF and $KMgF_3$. Their selection was based on structural compatibility, lattice parameters and electronic band alignment in the following systems: CaF_2 | Si/NaCl | CaF_2, $CsPbF_3$ | LiCl | $CsPbF_3$, KF | NaCl/LiCl | KF and $KMgF_3$ | NaCl/LiCl | $KMgF_3$. Our analysis of these systems was conducted using quantum-mechanical calculations within density functional theory (DFT), employing Quantum ESPRESSO (QE)[4] software suite. It was observed that the layer of atoms in the direct vicinity of the metallized compound played a crucial role in stabilizing the structure. For CaF_2, the lowest free energy was reached when fluorine atoms were close to the metallized nanolayer, whereas in the case of $KMgF_3$, the structure with NaCl between KF layers reached a lower energy than the analogous structure with NaCl between MgF_2 layers. Among the systems of interest, $KMgF_3$ | NaCl | $KMgF_3$ reached the highest stability with a band gap of 5.2 eV. This stability allowed us to dope this system, demonstrating high achievable doping levels of up to 0.3 e^- doping and 0.1 h^+ doping per atom. In the hole doping scenario, it was possible to achieve charge transfer to F^- (2p) orbitals with high density of states along with Cl^- (3p) orbitals. This phenomenon for fluorine is rarely achievable since fluorine serves mainly as an electron-withdrawing agent[5][6] and, in more stable structures, may lead to higher critical temperatures, which in this case was T_c = 68 mK. Electron doping primarily affected high-energy cationic K^+ (3d) and (4s), Mg^{2+} (3s) and Na^+ (3s) states, with a minor contribution from F^- orbitals. Better stability and higher doping level in this case resulted in a higher predicted critical temperature of 0.22 K at 0.2 e^- doping. In conclusion, for both e^- and h^+ doping, we successfully metallized NaCl using $KMgF_3$ as a wide band insulator. In the case of hole doping, F^- (2p) states were the main contributors to the electronic density of states.

References

[1] W. Grochala, *Wiadom. Chem. (Polish)*, **2021,** 75, 755.
[2] D. Jezierski et al., *PHYS CHEM CHEM PHYS,* **2022**, 24, 15705.
[3] A. Grzelak et al., *Angew. Chem. Int. Ed. Engl.*, **2021**, 60, 13892.
[4] P Giannozzi et al., *J. Phys.: Condens. Matter*, **2017**, 29, 465901.
[5] A. James, D. Murphy, S. Zahurak, *Nature*, **1989**, 338, 240.
[6] A. Bortolozo et al., *Mat. Sci. App.*, **2012**, 3, 623.

Application of CF_3-Nitrile Imines in the Synthesis of Unsymmetrical *N'*,*N'*-Trifluoroacetohydrazides

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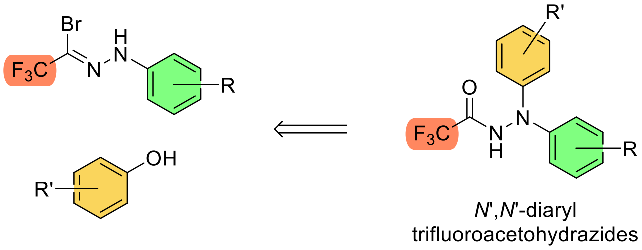
Although *N'*,*N'*-diaryl-acylhydrazide group occurs rarely in natural products, synthetic hydrazides of that type has been demonstrated as privileged structural motif of numerous pharmaceuticals and agrochemicals.[1] In addition, the mentioned hydrazides are convenient substrates for preparation of more complex heterocyclic systems including indazoles and benzo-1,2,4-triazines.[2] However, despite well-documented positive effects caused by introduction of fluoroalkyl groups into organic systems, fluorinated acylhydrazides are known to a limited extent. It is due to remarkable limitations of the classical synthetic methods comprising condensation of carboxylic acids (or derivatives) with appropriate hydrazines, catalytic Ullmann type *N*-arylations of readily available *N*-aryl-acylhydrazides, and azaphilic additions to azo compounds.[1-3] In continuation of our study on fluorinated 1,3-dipolar reagents,[4] here we report on efficient synthesis of unsymmetrical *N'*,*N'*-diaryl-trifluoroacetohydrazides based on a two-step protocol comprising trapping the *in situ* generated CF_3-nitrile imine with phenolate followed by Smiles rearrangement of the first formed hydrazonyl ester.



Scheme 1. Structures of target unsymmetrical hydrazides and key starting materials.

References
[1] (a) L. Deng, et al., *Org. Chem. Front.* **2024**, *11*, 1132; X. Han, et al., *J. Med. Chem.* **2016**, *59*, 2139; (c) V.N. Barinova, et al., *Pharm. Chem. J.* **1988**, *22*, 851.
[2] (a) J-Q. Zhang, et al., *Org. Biomol. Chem.* **2015**, *13*, 2055; (b) E.B. Elkaeed, J. An, A.M. Beauchemin, *J. Org. Chem.* **2017**, *82*, 9890.
[3] J. Yang, et al., *Org. Lett.* **2024**, *26*, 498; A.A. Berezin, et al., *J. Org. Chem.* **2014**, *79*, 314.
[4] (a) A. Kowalczyk, et al., *Org. Lett.* **2022**, *24*, 2499; (b) K. Świątek, et al., *Org. Lett.* **2023**, *25*, 4462; (c) G. Utecht-Jarzyńska, et al., *RSC Mechanochemistry* **2025**, *2*, 79.

Desulfurative Fluorination of Alkyl Phenyl Sulfides

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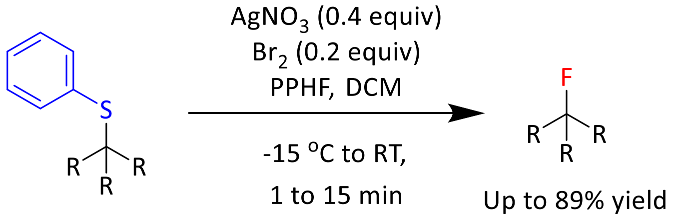
Fluorination of sp^3 carbons is an important transformation in medicinal and synthetic organic chemistry, allowing the manipulation of pharmacokinetic and pharmacodynamic properties of drug candidates, along with having applications in medical imaging through ^{18}F radiolabeling.[1]

Previous work in the Adamo group developed a suite of desulfurative halogenation methodologies achieving high yields and enantiospecifities.[2,3] Building on this work, and prior advancements in desulfurative fluorinations,[4] we present a novel methodology for late-stage fluorination with fast reaction times and a broad substrate scope (scheme 1). This approach achieves high yields even for complex substrates like amino acids and nucleotides, despite only requiring substoichiometric quantities of bromine and silver nitrate as co-reactants.



- ✓ Mild conditions
- ✓ Fast reaction times
- ✓ Broad functional group compatibility (38 substrates)

Scheme 1. Bromine and silver nitrate mediated desulfurative fluorination

References
[1] Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37* (2), 320–330.
[2] Canestrari, D.; Lancianesi, S.; Badiola, E.; Strinna, C.; Ibrahim, H.; Adamo, M. F. A. *Org. Lett.* **2017**, *19* (4), 918–921.
[3] Canestrari, D.; Cioffi, C.; Biancofiore, I.; Lancianesi, S.; Ghisu, L.; Ruether, M.; O'Brien, J.; Adamo, M. F. A.; Ibrahim, H. *Chem. Sci.* **2019**, *10* (39), 9042–9050.
[4] York, C.; Surya Prakash, G. K.; Olah, G. A. *Tetrahedron* **1996**, *52* (1), 9–14.

Expanding the Chemical Space of Pentafluorosulfanyl-containing Compounds

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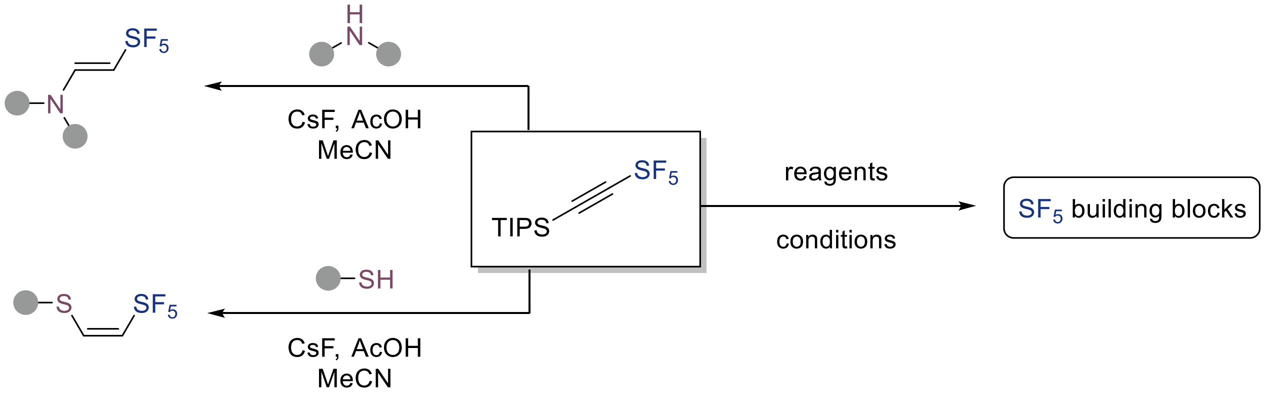
Compounds with pentafluorosulfanyl (SF_5) motif have unique electronic structures. They have shown unique physiological properties in lipophilicity, pKa, metabolic stability, and have emerged to be useful candidates for pharmaceutical, agrochemical and material industries. SF_5-containing compounds have also been suggested to be benign alternatives to per- and poly-fluoroalkyl compounds, which have caused potential hazards to the environment and health due to the poor bio-degradability and prolonged lifetime. However, synthetic access to a range of aliphatic and vinylated SF_5 scaffolds still remains a major challenge, due to reliance on toxic reagents and lack of mild and efficient reaction protocols. Recently, we became interested in the exploitation of prefunctionalised reagents to grant access to new classes of fundamental building blocks by downstream functionalisation.

Herein, we report novel transformations based on a simple silyl-protected SF_5-containing building block as the starting material to access a variety of novel classes of building blocks. We previously reported hydroamination and hydrothiolation reactions [1,2], employing mild conditions with good to excellent product yields. The newly accessed classes of molecules have shown remarkable chemical stability, and multiple handles on the molecules enable them to be further functionalised easily by employing simple procedures to expand the chemical space and synthetic utility of SF_5-containing compounds.



Scheme 1. Access to various SF_5 building blocks with a single substrate and beach-top conditions

References

[1] J. O. Wenzel, F. Jester, A. Togni, D. Rombach, *Chem. Eur. J.* **2024**, 30, e202304015 (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-brg1w).

[2] H. Kucher, J. O. Wenzel, D. Rombach, *ChemPlusChem* **2024**, 89, e202400168. (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-01jhn)

Semi-catalytic Trifluoromethylation using Tetrakis(trifluoromethylcopper)

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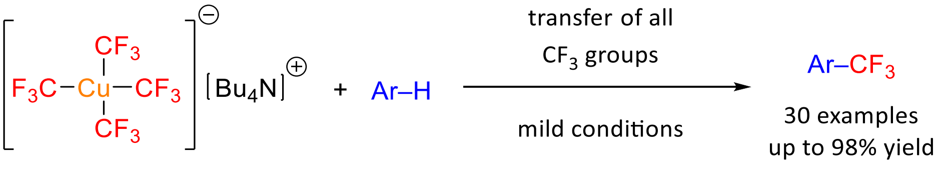
The trifluoromethyl group plays a crucial role in the pharmaceutical and agrochemical industries. The incorporation of the trifluoromethyl group into drug candidates can boost their chemical and metabolic stability and enhance properties, such as lipophilicity, bioavailability, and protein binding affinity.[1] Direct trifluoromethylation — especially when mediated or catalyzed by transition metals — represents one of the most promising and efficient approaches. Generally, the trifluoromethyl group can be introduced into organic molecules via nucleophilic, electrophilic, or free radical mechanisms.[2]

Organocopper(III) species are widely regarded as essential intermediates in various cross-coupling reactions, aerobic oxidations, and enzyme-catalyzed processes. However, these complexes are typically thermally unstable and difficult to isolate, which presents significant challenges for both their study and practical implementation.[3]

The trifluoromethyl group stands out as a unique class of ligands capable of stabilizing high-valent organocopper(III) species. Trifluoromethyl copper(III) complexes have proven effective for C–H trifluoromethylation of arenes, alkenes, alkynes, and C(sp^3)–H bonds.[3–5] One of the most extensively studied compounds in this class is $[Cu(CF_3)_4][Bu_4N]$, which is generally considered inert as a trifluoromethylation agent.[6] Here we present the first application of $[Cu(CF_3)_4][Bu_4N]$ for trifluoromethylation reactions, capable of transferring up to four trifluoromethyl groups.



Scheme 1. The application of $[Cu(CF_3)_4][Bu_4N]$ for trifluoromethylation reactions.

References

[1] Kirsch, P. Modern Fluoroorganic Chemistry, WILEY-VCH, **2004**.
[2] Chu, L.; Qing, F. L. *Acc. Chem. Res*. **2014**, *47*, 1513–1522.
[3] Liu, H.; Shen, Q. *Coord. Chem. Rev*. **2021**, *442*, 213923.
[4] Motornov, V.; Klepetářová, B.; Beier, P. *Adv. Synth. Catal*. **2023**, *365*, 2858–2864.
[5] Motornov, V.; Procházka, M.; Alpuente, N.; Salvador, P.; Slavíček, P.; Klepetářová, B.; Ribas, X.; Beier, P. *ChemistryEurope* **2024**, *2*, e202400004.
[6] Alayoglu, P.; Chang, T.; Yan, C.; Chen, Y. S.; Mankad, N. P. *Angew. Chem., Int. Ed.* **2023**, *62*, e202313744.

Investigation of Dicationic Ionic Liquids with Difluorophosphate Anion

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Hwang Jinkwang,[1] *Matsumoto Kazuhiko*[1]

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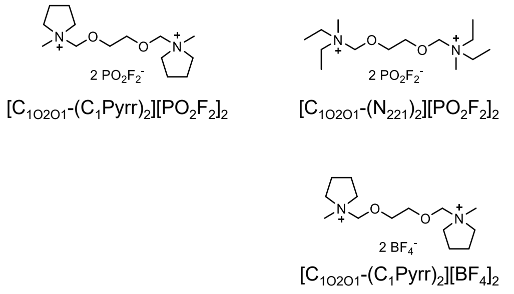
Recently, dicationic ionic liquids (DILs) have gained attention as electrolytes in secondary batteries. Compared to conventional monocationic ionic liquids (MILs), DILs can exhibit enhanced thermal stability and a broader electrochemical window. However, the larger molecular size and double charge of the cation tend to increase viscosity and melting point of the DILs, which can impact their practical application. Viscosity is a particularly critical factor for electrolytes, as lower viscosity is related to ionic conductivity and cell fabrication. Previous studies on piperidinium-based MILs have shown that introduction of the ether linker structure effectively reduces viscosity. [1]

Ionic liquids with difluorophosphate anion ($PO_2F_2^-$) were synthesized and characterized in a previous study. [2] In addition to low melting point and viscosity, $PO_2F_2^-$-based ionic liquids provide a high polarity owing to the large dipole moment on the anion.

This study explores the introduction of the oxygen into the linker of the dication in addition to the incorporation of $PO_2F_2^-$ in order to obtain DILs with low melting point and viscosity. The resulting physical properties are compared with the physical properties of those with other fluorocomplex anions. (**Figure 1**)



	T_g/ °C	ρ/ g cm^{-3}	η/ mPa s	σ/ mS cm^{-1}	EW/ V
$[C_{1O2O1}\text{-}(C_1Pyrr)_2][PO_2F_2]_2$	−73	1.349	2000	0.42	4.91
$[C_{1O2O1}\text{-}(N_{221})_2][PO_2F_2]_2$	−68	1.277	3700	0.22	4.27
$[C_{1O2O1}\text{-}(C_1Pyrr)_2][BF_4]_2$	−49	1.305	11900	0.13	4.91

Figure 1. Structures and physical properties of dicationic ionic liquids.

References

[1] T. Nokami, T. Yamashita, T. Komura, N. Handa, M. Shimizu, K. Yamaguchi, Y. Domi, H. Usui, H. Sakaguchi, and T. Itoh, *Faraday Discuss*., 2018, 206, 523.
[2] K. Matsumoto, R. Hagiwara, Inorg. Chem., 2009, 48, 7350.

From Trifluoromethyl to Pentafluoroethyl: New Approaches in Gold(III) Complexes Stabilization

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In the last two decades the organometallic chemistry of gold has undergone significant developments, both in oxidation states I and III. Despite that, stabilization of Au(III) species is not always straightforward. A synthetic strategy for achieving this is based on the use of polydentate ligands such as P^C, N^C, C^N^C, or N^C^C.[1] Alternatively, the use of trifluoromethyl as a ligand has proven to be an effective tool for the development of this chemistry. In general, the marked group electronegativity of CF_3 and its relatively small size facilitate the stabilization of *late* transition metal complexes in high oxidation states.[2] Although diverse Au(III) trifluoromethyl complexes have been reported, their analogues containing longer perfluoroalkyl chains remain scarce.[3]

Recently, in our research group, a wide range of Au(III) complexes stabilized by trifluoromethyl ligands have been prepared, with general formulae $[PPh_4][Au^{III}(CF_3)_2(X)_2]$, $[PPh_4][Au^{III}(CF_3)_3(X)]$ (X = F, Cl, Br, I, CN), and $[Au^{III}(CF_3)_3L]$ (L = NCMe, OEt_2, CN^tBu, py, PR_3, tht).[4] Now, we have focused our attention on longer perfluoroalkyl ligands, in particular the pentafluoroethyl. In this communication we report the synthesis and characterization of novel Au(III) complexes stabilized by C_2F_5 ligands.

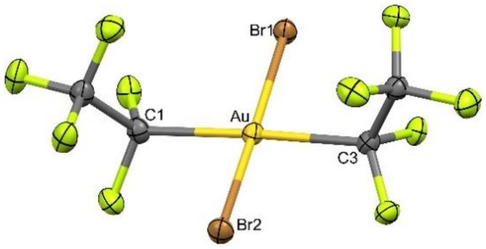

Figure 1. X-Ray structure of the $[PPh_4][Au(C_2F_5)_2Br_2]$ complex.

References

[1] a) Herrera, R. P.; Gimeno, M. C. *Chem. Rev.* **2021**, *121*, 8311-8363. b) Rocchigiani, L.; Bochmann, M. *Chem. Rev,* **2021**, *121*, 8364-8451.
[2] García-Monforte, M. A.; Martínez-Salvador, S.; Menjón, B. *Eur. J. Inorg. Chem*. **2012**, 4945-4966.
[3] a) Portugués, A.; López-García, I.; Jiménez-Bernad, J.; Bautista, D.; Gil-Rubio, J. *Chem. Eur. J.* **2019**, *25*, 15535-15547. b) Rachor, S. G.; Müller, R.; Wittwer, P.; Kaupp, M.; Braun, T. *Inorg. Chem*. **2022**, *61*, 357-367.
[4] a) Martínez-Salvador, S.; Falvello, L. R.; Martín, A.; Menjón, B. *Chem. Eur. J.* **2013**, *19*, 14540-14552. b) Pérez-Bitrián, A.; Baya, M.; Casas, J. M.; Martín, A.; Menjón, B.; Orduna, J. *Angew. Chem. Int. Ed*. **2018**, *57*, 6517-6521. c) Pérez-Bitrián, A.; Martínez-Salvador, S.; Baya, M.; Casas, J. M.; Martín, A.; Menjón, B.; Orduna, J. *Chem. Eur. J.* **2017**, *23*, 6919-6929. d) Pérez-Bitrián, A.; Baya, M.; Casas, J. M.; Falvello, L. R.; Martín, A.; Menjón, B. *Chem. Eur. J.* **2017**, *23*, 14918-14930.

The Bioinorganic Impact of Fluorine Studied by Vibrational Spectroscopy

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ATCUN peptides are histidine-containing tripeptides with metalloenzyme properties in their metal-bound form. For instance, their cobalt (Co) complexes have catalytic activity for hydrogen production and nitrite reduction.

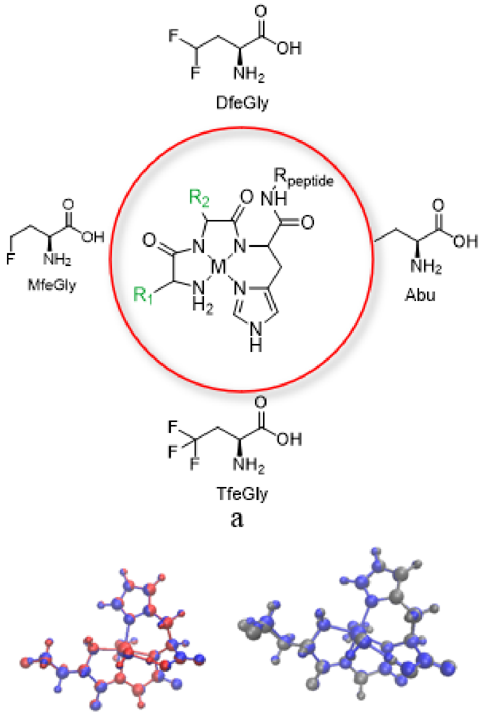

Figure 1. (a) Architecture of (fluorinated) ATCUN complexes. (b and c) Structural impact of mono- and difluorination.

Here, we studied Co complexes of ATCUN peptides containing (non-)fluorinated amino acids. Four different residues (amino-acid side chains) were placed in positions R_1 and R_2 (Fig. 1 a). Using infrared (IR) and resonance Raman spectroscopy supported by DFT-based anharmonic frequency calculations, we examined the vibrational modes of the complexes to understand the impact of fluorination and lay a foundation for nonlinear IR experiments.

C-F stretching vibrations are valuable markers for studying fluorination, expected in the 1100-1300 cm^{-1} region. However, IR spectra showed no significant differences between fluorinated and non-fluorinated complexes, and computational investigations revealed that these vibrations appear at unusually low frequencies <1000 cm^{-1}. We ascribe this observation to metal binding. Moreover, fluorine has a high electronegativity and hydrophobicity, which typically causes significant changes in the structures of peptides. We compared the computed structures and vibrational properties of monofluorinated (red; b) and difluorinated variants (grey; c) with the nonfluorinated analogue (blue; b & c). Surprisingly, structural and spectroscopic changes were negligible, which points towards a high rigidity of the chelating peptide scaffold, supporting a significant impact of metal-binding on fluorinated peptides. Of note, the potential of fluorinated amino acids as hydrogen-bond donors or acceptors and their influence on microsolvation in biocatalytic metal centres is of high interest. The above insight indicates that these aspects can be studied independently from other effects of fluorination. Initial insights based on vibrational spectroscopy and DFT calculations, using both implicit and explicit solvation models, will be provided.

References

[1] Kandemir et al., Inorg. Chem. 2016, 55, 1355−1357

Functionalization of Nanodiamonds with Perfluoropolyether Peroxide *Via* a Facile Thermochemical Process

Davide Ceriotti[a], *Piergiorgio Marziani*[a], *Luca Magagnin*[a,b],
Elodie Petit[c], *Samar Hajjar-Garreau*[d], *Julien Parmentier*[d], *Marc Dubois*[c]*, *Maurizio Sansotera*[a,b]*

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The functionalization of nanodiamonds (NDs) and fluorinated nanodiamonds (F-NDs) with perfluoropolyether (PFPE) peroxide was achieved through a thermal process, enhancing their surface properties. Fourier-transform infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance (NMR) spectroscopy confirmed the successful attachment of PFPE moieties, while X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) quantified the degree of functionalization. Water contact angle measurements demonstrated a significant increase in hydrophobicity compared to pristine materials, showing superhydrophobic behaviour on F-NDs. These findings provide valuable insights into the surface chemistry of PFPE-functionalized nanodiamonds and highlight their potential for application in systems requiring extreme hydrophobicity and enhanced chemical resistance.

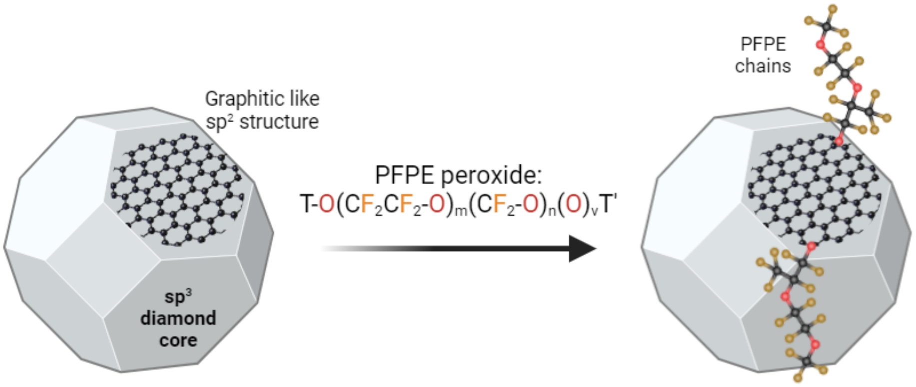

Figure 1. Nanodiamonds functionalization with perfluoropolyether peroxide graphical representation.

Reference

[1] Ceriotti, D., Marziani, P., Magagnin, L., Sansotera, M., Petit, E., Hajjar-Garreau, S., Dubois, M. Functionalization of Nanodiamonds with Perfluoropolyether Peroxide Via a Facile Thermochemical Process. Available at SSRN 493884 [*Submitted, under peer review*]

Scientific Programme: Talks

Friday, August 8th, 2025

Friday, August 8th, 2025

PLENARY SESSION - FLORIAN KRAUS

Room: Auditorium II
Chair: Berthold Hoge, Bielefeld University, Germany

09:00 – 10:00	**OXIDATION OF HALOGEN PENTAFLUORIDES AND N_2**
PL	**Florian Kraus**, Philipps-Universität Marburg, Germany

KEYNOTE SESSION - CORMAC MURPHY

Room: Auditorium II
Chair: Marie-Pierre Krafft, Institut Charles Sadron (UPR 22), University of Strasbourg, France

10:00 – 10:45	**MICROBIAL ENZYMES THAT DEGRADE PFAS**
KN	**Cormac D. Murphy**, University College Dublin, Ireland

KEYNOTE SESSION - KAZUHIKO MATSUMOTO

Room: Auditorium II
Chair: Michael Gerken, University of Lethbridge, Canada

11:15 – 12:00	**FLUORINE CHEMISTRY IN ENERGY APPLICATIONS**
KN	**Kazuhiko Matsumoto**, Kyoto University, Japan

PLENARY SESSION - PETR BEIER

Room: Auditorium II
Chair: Henryk Koroniak, Adam Mickiewicz University, Poland

12:00 – 13:00	**FLUORINATED ORGANIC AZIDES IN SYNTHESIS AND BIOCONJUGATION**
PL	**Petr Beier**, Institute of Organic Chemistry and Biochemistry, Czech Republic

CLOSING SESSION AND AWARDS

Room: Auditorium II

13:00 – 14:30	**CLOSING SESSION & AWARDS**
	Ana B. Pereiro and João M. M. Araújo, NOVA FCT, Portugal
	Presentations of the next ESFC (Czech Republic) and ISFC (France)
	Award ceremony for the best posters
	Closing words

Scientific Programme: Posters

Wednesday, August 6th, 2025

17:30 – 19:30

Scientific Programme: Posters

Wednesday, August 6th, 2025: 17:30–19:30

Room: Pavilion 3

ORGANIC CHEMISTRY

P01	**RADICAL PHOTOCHEMICAL DIFLUOROSULFOXIMINATION OF ALKENES AND PROPELLANES** **Julien Paut**, University of Paris-Saclay, France
P03	**SYNTHESIS OF HFIP ESTERS VIA DEFLUORINATION OF AROMATIC TRIFLUOROMETHYL GROUPS** **Shoki Hoshikawa**, Setsunan University, Japan
P04	**STRAIN-RELEASE-DRIVEN SYNTHESIS OF PERFLUOROSULFANYLATED FOUR-MEMBERED RINGS UNDER ENERGY TRANSFER PHOTOCATALYSIS** **Lulu Han**, Université Claude Bernard Lyon 1, France
P05	**DECOMPOSITION OF PTFE BY THE VIBRATION MILL** **Shiina Yasugami**, Daikin Industries, LTD, Japan
P06	**MECHANOCHEMICAL DIFLUOROMETHYLATION WITH HYPERVALENT IODINE REAGENTS** **Vitalii Solomin**, University of Rouen Normandy, France
P07	**S_NAR REACTIONS OF PHENOL DERIVATIVES WITH FLUOROBENZENE** **Feng Wang**, Roskilde University, Denmark
P08	**PYRIDINIUM-BASED FLUOROSULFONAMIDE REAGENTS ENABLED PHOTOREDOX-CATALYZED RADICAL FLUOROSULFONAMIDATION** **Chao Sun**, Nanjing University, China
P09	**THE REACTIVITY OF TETRAFLUORO(TRIFLUOROMETHYL)-λ^6-SULFANYL CHLORIDE (CF_3SF_4Cl) WITH SUBSTITUTED ALKYNES AND REACTIONS OF THE ADDUCTS FORMED** **Elleanor van der Riet**, University at Albany, USA
P10	**THE INFLUENCE OF *N*-(2-(TETRAFLUORO(TRIFLUOROMETHYL)-λ^6-SULFANYL) ETHYL)(*N*-CF_3SF_4-ETHYL) GROUPS ON PEPTIDE BOND FORMATION AND AMIDE BOND CONFORMATION.** **Willow M. Desoucey**, University at Albany, USA
P11	**THE APPLICATION OF SULFUR HEXAFLUORIDE IN SYNTHETIC CHEMISTRY FOR PENTAFLUOROSULFANYLATION** **Sven Klehenz**, Karlsruhe Institute of Technology, Germany
P12	**EXPANDING THE CHEMICAL SPACE OF PENTAFLUOROSULFANYL-CONTAINING COMPOUNDS** **Lujie Xu**, University of Zurich, Switzerland
P13	**NOVEL HEXAFLUOROSULFUR ACTIVATION UTILIZING AN ORGANIC PHOTOREDOX CATALYST** **Max Flügge**, Karlsruhe Institute of Technology, Germany
P14	**INVESTIGATING DNA BINDING OF ALL-*CIS* PENTAFLUOROCYCLOHEXANES USING FRET**

	George Kingsley-Moore, University of St Andrews, UK
P15	**PHOTO-CATALYTIC SYNTHESIS OF FLUORINATED SUPERACIDIC CARBON ACIDS** **Rikuto Fujimoto**, Tokyo University of Pharmacy and Life Sciences, Japan
P16	**SYNTHESIS AND PROPERTIES OF SELECTIVELY FLUORINATED *TERT*-LEUCINE DERIVATIVES** **Josephine M. Stewart**, University of St Andrews, UK
P17	**UNLOCKING THE PENTAFLUOROSULFANYLATION REACTIVITY OF SF$_6$ BY PHOTOREDOX CATALYSIS** **David Rombach**, University of Zurich, Switzerland
P18	**SYNTHESIS OF α,α-DIFLUORO-β-THIOCARBOXYLATES FOR A CYSTATIN-FREE CHEMICAL LIGATION** **Atsushi Tarui**, Setsunan University, Japan
P19	**ROOM TEMPERATURE IONIC LIQUIDS – ADVANCED REACTION MEDIA FOR ORGANIC SYNTHESES WITH HIGHLY REACTIVE CHEMICALS – LET'S MAKE FLUORINATION SAFER** **Nicolai V. Ignatyev**, Universität Würzburg, Germany
P20	**APPLICATION OF CF$_3$-NITRILE IMINES IN THE SYNTHESIS OF UNSYMMETRICAL *N*,*N*-TRIFLUOROACETOHYDRAZIDES** **Adrian Warcholiński**, University of Lodz, Poland
P21	**SYNTHETIC STRATEGIES LEVERAGING FLUORIDE-ENABLED REACTIVITY AND SELECTIVITY** **Christine M. Le**, York University, United Kingdom
P22	**BICYCLO[1.1.1]PENTANES WITH FLUORO AND FLUOROALKYL SUBSTITUENTS: REDOX-ACTIVE ESTERS AND THEIR REACTIVITY** **Stacie K. Nelson**, University of Lethbridge, Canada
P23	**DEVELOPMENT OF PERFLUORO ALKOXYLATION REAGENTS AND SYNTHESIS OF PERFLUOROALKYL ETHERS** **Moe Fujishiro (Hosokawa)**, Daikin Industries, LTD, Japan
P24	**HIGHLY SELECTIVE SYNTHESIS OF REGIO- AND STEREOISOMERS OFFLUOROALKYLATED 1,3-ENYNES BY OPTIMAL USE OF CATALYST** **Yuta Kabumoto**, Kyoto Institute of Technology, Japan
P25	**STEREO- AND REGIOSELECTIVE VICINAL FLUOROSULFONYL-BORYLATION OF UNSATURATED HYDROCARBONS** **Heyin Li**, Nanjing University, China
P26	**DESULFURATIVE FLUORINATION OF ALKYL PHENYL SULFIDES** **Brian Durkan**, Royal College of Surgeons, Ireland
P27	**VISIBLE-LIGHT-MEDIATED TRIFLUOROMETHYLATION/RING CLOSURE SEQUENCES OF 2-VINYL PHENOLS: SYNTHESIS OF TRIFLUOROMETHYLATED 4*H*-CHROMENE DERIVATIVES** **Dae Young Kim**, Soonchunhyang University, South Korea
P28	**THE SYNTHESIS OF *N*-SUBSTITUTED HYDROXAMIC ACIDS VIA A PENTAFLUOROPYRIDINE MEDIATED PROCEDURE** **Daniel E. Bonn**, Durham University, United Kingdom
P29	**MILD C-F ACTIVATION OF PERFLUOROALKYL SUBSTANCES BY α-FLUORINE SUBSTITUTION OF PERFLUOROALKYL AZIDES WITH THIOLS** **Olena Shaitanova**, Academy of Sciences of the Czech Republic, Czechia

P82 **USE OF CYCLIC SULFOXIMINES AS (DEUTERO)(FLUORO)METHYLATION REAGENTS**

Gabriel Goujon, Institut Lavoisier de Versailles - UVSQ, France

P83 **DIAMINOMETHYLATION OF FLUOROPYRIDINES**

Aleksandr Kostyuk, Institute of Organic Chemistry, Ukraine

ORGANOMETALLIC CHEMISTRY

P30 **BENZIMIDAZOLE-2-YLIDENE-SILVER(I) COMPLEXES BEARING THE 4-TRIFLUOROMETHOXY GROUP AS ORGANOFLUORINE COMPOUNDS: SYNTHESIS, CHARACTERIZATION, AND INHIBITORY PROPERTIES AGAINST SOME METABOLIC ENZYMES**

Yetkin Gök, Inonu University, Turkey

P31 **SYNTHESIS AND CHARACTERIZATION OF PD(II) METAL COMPLEXES DERIVED FROM N-HETEROCYCLIC CARBENES WITH FLUORINATED SUBSTITUENTS**

Burcu Tezcan, Çukurova University, Turkey

P32 **FROM TRIFLUOROMETHYL TO PENTAFLUOROETHYL: NEW APPROACHES IN GOLD(III) COMPLEXES STABILIZATION**

Alba de Toro, Universidad de Zaragoza CSIC, Spain

P33 **ACTIVATION OF PERFLUORO(METHYL VINYL ETHER) AT Rh(I) PHOSPHINE COMPLEXES: METAL-CENTERED VERSUS PHOSPHINE MEDIATED DECARBONYLATION**

Soodeh Mollasalehi, Humbold-Universität zu Berlin, Germany

P34 **SEMI-CATALYTIC TRIFLUOROMETHYLATION USING TETRAKIS(TRIFLUOROMETHYLCOPPER)**

Petr Pospíšil, Czech Academy of Sciences, Czechia

P35 **PENTAFLUOROETHYL STABILIZED α-SILYL CARBANIONS**

Julia Landwehrmann, Universität Bielefeld, Germany

INORGANIC CHEMISTRY

P36 **NOVEL READILY AVAILABLE LANTHANIDE-HALIDE COMPLEXES AS POTENTIAL PRECURSORS TO SINGLE MOLECULE MAGNETS**

Magdalena Abramowicz, University of Warsaw, Poland

P37 **HYDRODEFLUORINATION WITH HETEROGENOUS ZIEGLER-NATTA CATALYSTS**

Diego De Canditiis, Università degli Studi di Napoli Federico II, Italy

P38 **SYNTHESIS OF FLUORINATED Zn(II) COORDINATION 2D SHEETS WITH ADAPTIVE PORE STRUCTURES FOR π-HOLE-INDUCED GUEST ENCAPSULATION**

Akiko Hori, Shibaura Institute of Technology, Japan

P39 **SYNTHESIS AND APPLICATION OF THE WEAKLY COORDINATING ANION $[CHB_{11}F_{11}]^-$**

Johanna Drolshagen, Universität Freiburg, Germany

P40 **FROM STABLE HALOGENATED SUPERELECTROPHILIC TRITYLCATIONS TO CORRESPONDING LUMINESCENT TRITYLRADICALS AND THEIR PEROXIDES**

Johanna Schlögl, Freie Universität Berlin, Germany

P41 **$CF_3OCH_2C(O)OH$ AND $(CF_3)_2NCH_2C(O)OH$ – TWO PARTIALLY FLUORINATED ACIDS**

Sabine Lorenzen, University Würzburg, Germany

P42 **BIS(PERFLUOROORGANYL)DISELANES AND -DITELLANES**

Kjell Simon Krauser, Universität Bielefeld, Germany

P43 **FLUORIDE-ION DONOR PROPERTIES OF $MoOF_4$ AND WOF_4**

Craig W. Sommer, University of Lethbridge, Canada

P44 **NEW SYNTHETIC ROUTES FOR ARYLXENONIUM(II) SALTS AND STUDY OF THEIR LEWIS ACIDITY**

Pablo Cortés Soláns, Humboldt-Universität zu Berlin, Germany

P45 **PLATINUM-CATALYSED HYDROFLUORINATION OF ALKYNES PROMOTED BY A FLUORIDE SHUTTLE**

Ouchan He, Humboldt-Universität zu Berlin, Germany

P46 **C–F bond activation of Fluoroalkanes *via* Germylium Ions catalysis**

Julie Borel, Humboldt Universität zu Belrin, Germany

P47 **INCREASING THE OXIDATION STRENGTH OF POLYNITRILE OXIDIZERS BY COORDINATION TO LEWIS ACIDS AND SYNTHESIS OF A NEW STRONG LEWIS ACID**

Amina L. Moshtaha, Freie Universität Berlin, Germany

P48 **SILVER FLUORIDES IN MIXED OXIDATION STATES (I)/(II)**

Katarzyna Kuder, University of Warsaw, Poland

BIOORGANIC & MEDICINAL CHEMISTRY

P49 **HOW DOES FLUORINE REALLY AFFECT THE PERFORMANCE OF PHARMACEUTICALS?**

Graham Pattison, University of Lincoln, United Kingdom

P50 **SURFACE ENHANCED INFRARED ABSORPTION SPECTROSCOPY ON THE INTERACTION OF CELL PENETRATING PEPTIDES WITH LIPID BILAYERS**

Ferhat Mutlu, Freie Universität Berlin, Germany

P51 **INVESTIGATING THE SITE-SPECIFIC IMPACT OF FLUORINE SUBSTITUTION ON AROMATIC INTERACTIONS IN A TRYPTOPHAN ZIPPER PEPTIDE**

David Reiter, Freie Universität Berlin, Germany

MATERIALS

P52 **POST-METAL-ETCH HF CONDITIONING OF BCAT GATE OXIDE FOR SIMULTANEOUS GIDL SUPPRESSION AND WORD-LINE RESISTANCE RECOVERY IN SUB-10 NM DRAM**

Jeon Jaehyeon, Sungkyunkwan University, South Korea

P53 **FLUORINE GAS GENERATION WITH METAL FLUORIDE REDUCTION**

Yuki Shukuno, Kyoto University, Japan

P54 **FUNCTIONALIZATION OF NANODIAMONDS WITH PERFLUOROPOLYETHER PEROXIDE *VIA* A FACILE THERMOCHEMICAL PROCESS**

Davide Ceriotti, Politecnico di Milano, Italy

P55 **MECHANOCHEMICAL SYNTHESIS OF FLUORINATED PEROVSKITES $KCuF_3$ and $KNiF_3$**

Arianna Collora, Politecnico di Milano, Italy

P56 **INVESTIGATION OF DICATIONIC IONIC LIQUIDS WITH DIFLUOROPHOSPHATE ANION**

	Kentaro Kamada, Kyoto University, Japan
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Gabriel Zarca, Universidad de Cantabria, Spain

Organic Chemistry

Radical Photochemical Difluorosulfoximination of Alkenes and Propellanes

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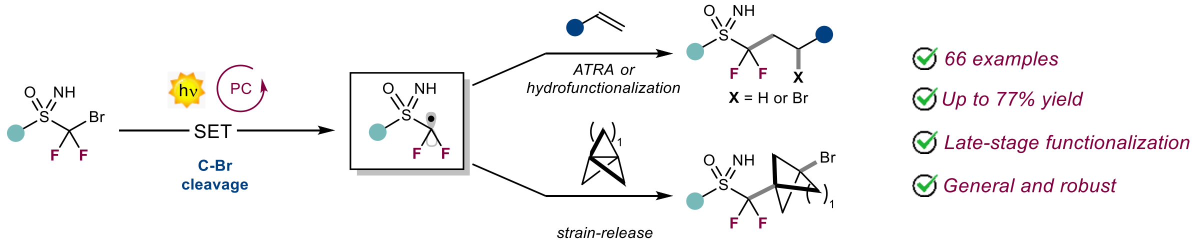
Sulfoximines are promising moieties for their bioisosteric replacement of sulfones.[1] Theses compounds possess interesting properties such as high chemical stability, increased solubility in water and multiple hydrogen bond donor/acceptor sites. Further, the N-atom adds value to the structure from a sulfone by adding intrinsic chirality and the possibility to explore the 3D-chemical space with exit vectors. On the other hand, the unique effect of the fluorine atom on physical and biological properties of chemicals, organofluorine chemistry holds a central role in various areas, with many applications in materials, agrochemical, and medicinal chemistry. Especially in medicinal sciences, the fluorine atom shown in many cases, an increasing bioavailability with respect to their original non fluorinated versions.[2] We thus may hypothesize that S-perfluoroalkylated sulfoximines would have a dual advantage in terms of properties. However, the installation of the sulfoximine unit into a substrate in one pot is quite challenging and not very explored in literature.

Here, we report for the first time, a new method of sulfoximination by C-C bond of olefins and propellanes enabled by a metal-free photocatalysts. The process is general, robust and tolerates diverse functional groups, including esters, ketones, double bond, silyl groups and boronic esters. The rationalization of divergent reaction mechanism performing Stern-Volmer quenching and EPR experiments revealed the key activity of a difluoroalkyl sulfoximine radical.



Scheme 1. Light-driven difluorosulfoximination of alkenes and propellanes

References

[1] Baldone, S.; Paut, J.; Anselmi, E.; Dagousset, G.; Tuccio, B.; Pelosi, G.; Cuadros, S.; Magnier, E.; Dell'Amico, L. *Chem. Sci.* **2025**, *16*, 6957.

Synthesis of HFIP Esters via Defluorination of Aromatic Trifluoromethyl Groups

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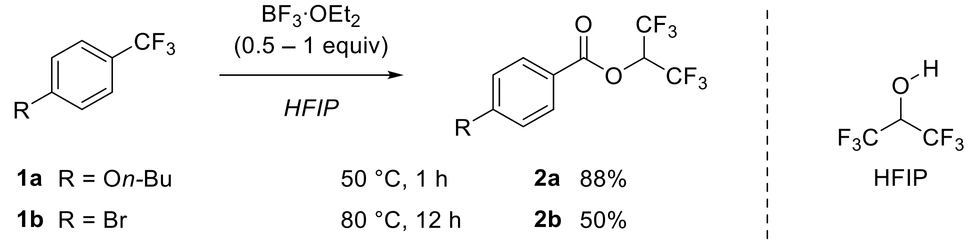
The trifluoromethyl (CF_3) group is a robust, strongly electron-withdrawing, and highly lipophilic substituent that significantly alters the physical and electronic properties of organic molecules. These features have made it indispensable in fields such as pharmaceutical and materials science, motivating the continued development of methods for its incorporation. In contrast, selective transformation of CF_3 groups remains a major synthetic challenge, as the C–F bond is exceptionally strong and resists activation under conventional conditions.

Herein, we report that benzotrifluoride derivatives can be efficiently converted into 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) esters by treatment with a Lewis acid (e.g., $BF_3 \cdot OEt_2$) in HFIP as the solvent. The reaction proceeds via defluorination of the CF_3 group followed by nucleophilic trapping by HFIP. Owing to their reactivity as activated esters, HFIP esters are attractive intermediates for further derivatization.[1,2] However, existing synthetic routes typically require corrosive acid chlorides or directing-group-assisted C–H activation, which limits both practicality and substrate scope.

For example, treatment of 4-butoxybenzotrifluoride **1a** with 0.5 equivalents of $BF_3 \cdot OEt_2$ in HFIP afforded the corresponding HFIP ester **2a** in 88% yield (Scheme 1). The reaction also proceeded with substrates bearing electron-withdrawing groups such as a bromine atom, giving product **2b** in 50% yield under mild heating conditions. To explore the synthetic utility of the products, we examined the HFIP ester moiety as a versatile reaction point for a range of transformations, including cross-coupling reactions. In this communication, we will present a convenient method for HFIP ester synthesis via a novel CF_3 group transformation, along with its potential for broader synthetic applications.



Scheme 1. Synthesis of HFIP esters via defluorination of benzotrifluorides.

References

[1] Kelly, C. B.; Mercadante, M. A.; Wiles, R. J.; Leadbeater, N. E. *Org. Lett.* **2013**, *15*, 2222.
[2] Vatèle, J.-M. *Synlett*, **2015**, *26*, 2280.

Strain-Release-Driven Synthesis of Pentafluorosulfanylated Four-Membered Rings under Energy Transfer Photocatalysis

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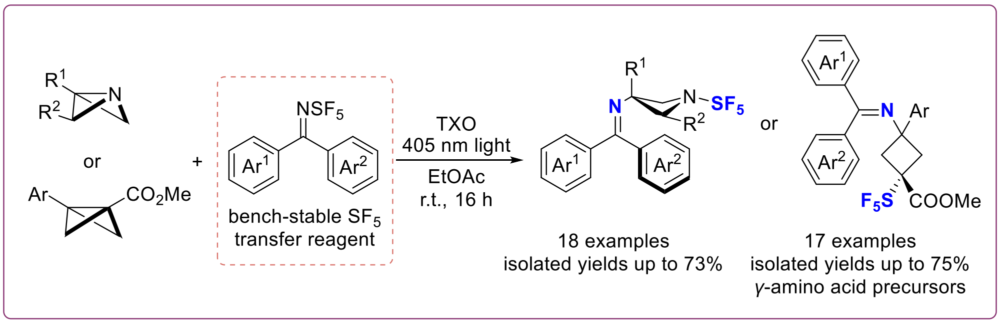
Methods to prepare SF_5-containing molecules are of significant interest, as the pentafluorosulfanyl (SF_5) group imparts unique chemical and physical properties—such as high electronegativity, lipophilicity, and thermal stability—that are valuable in pharmaceuticals, agrochemicals, and materials science.[1] On the other hand, four-membered rings play a crucial role in molecular design. The three-dimensional shape of these rings is of particular importance, as their compact, rigid structure induces conformational constraints, enhancing their ability to interact more effectively and selectively with biological targets.[2] The use of our shelf-stable reagent,[3] imine-SF_5, enables selective access to four-membered ring SF_5-containing molecules under mild reaction conditions via a strain-release approach facilitated by energy-transfer catalysis. Mechanistic investigations provided insight into the reaction pathway. This approach advances pentafluorosulfanylation methodology, paving the way for future development (**Scheme 1**).[4]



References

[1] Sowaileh, M. F.; Hazlitt, R. A.; Colby, D. A. *ChemMedChem*. **2017**, *12* (18), 1481.
[2] Kraemer, Y.; Buldt, J. A.; Kong, W. Y.; Tantillo, D. J.; Pitts, C.R. et al. *Angew. Chem. Int. Ed.* **2024**, *63*, e202319930.
[3] YANG, Y.; HAN, L.; Taponard, A.; Khrouz, L.; Bucher, C.; Cyrille, M.; Médebielle, M.; Tlili, A. *Angew. Chem. Int. Ed.* **2025**, e202505146
[4] Tlili, A.; HAN, L.; YANG, Y.; Canavero, L.; Brettnacher, L.; Khrouz, L.; Cyrille, M.; Médebielle, M.; *ChemRxiv.* **2025-04-28**, DOI:10.26434/chemrxiv-2025-6z4c6

Decomposition of PTFE by the Vibration Mill

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Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer renowned for its exceptional properties, including its low friction coefficient, non-stick characteristics, and outstanding electrical insulation. It boasts a high melting point and remarkable resistance to chemicals, making PTFE a material of choice in diverse applications ranging from non-stick cookware to crucial industrial components. Its superior heat and chemical resistance qualify it for widespread use across various industries. However, these very properties pose challenges for its decomposition, resulting in slower recycling progress compared to other resins.

In PTFE recycling, methods such as chemical recycling aim to revert it to monomer form, requiring heating above 600°C. On the other hand, the mechanochemical approach utilizes mechanical energy to promote chemical reactions different from conventional ones [1]. This approach can reduce reliance on extreme thermal conditions, lower energy consumption, reduce costs, diminish environmental impact, and offer a potential alternative to traditional decomposition methods. Particularly, Saito et al. have reported the use of this mechanochemical approach, employing CaO, to decompose PTFE at room temperature [2]. However, their research utilized a planetary ball mill, presenting challenges for scale-up. In our study, we explored the decomposition of PTFE using a vibration mill apparatus, which allows for scale-up, and we report the details of our findings.

$$(CF_2\text{-}CF_2)_n \xrightarrow{CaO} CaF_2 + CaO + C + CO$$

Scheme 1. PTFE decomposition by CaO

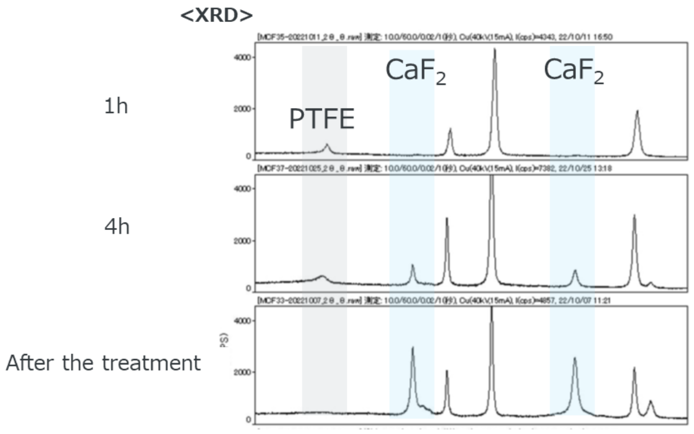

Figure 1. XRD pattern of PTFE mixture for different times

References

[1] Keisuke Kondo, Koji Kubota, and Hajime Ito, *RSC Mechanochem.*, **2025**, *2*, 389.
[2] Jun Qu, Xiaoman He, Qiwu Zhang, Xinzhong Liu and Fumio Saito, *Environmental Technology*, **2017**, *38 (11),* 1421.

Mechanochemical Difluoromethylation with Hypervalent Iodine Reagents

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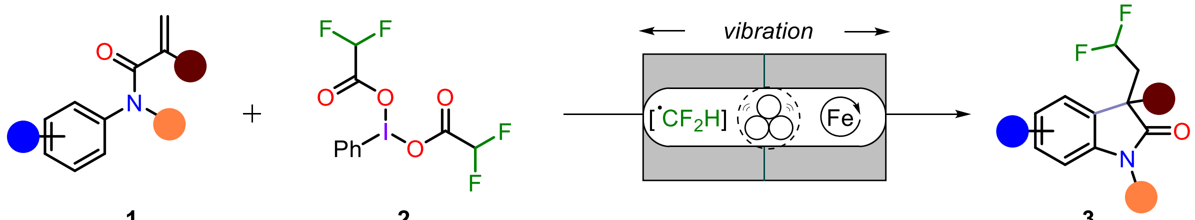
The difluoromethyl group (-CF_2H) is well-known for its importance in medicinal chemistry applications. It can play the role of lipophilic hydrogen bond donor and, consequently, act as a bioisostere of alcohols and thiols.[1] Radical difluoromethylation strategy was widely applied to achieve CF_2H-substituted compounds traditional solution-based syntheses with good yields.[2] Nevertheless, difluoromethylation in mechanochemical setup is currently limited to heteroatoms modifications,[3] whereas direct C–CF_2H bond formation is still lacking. After our initial success regarding ball-milling radical trifluoromethylation,[4] we sought to study the usage of iodonium regents to perform difluoromethylation under solvent-free conditions. Utilizing readily available iodosobenzene difluoroacetate **2** as a source of CF_2H radical, it was possible to achieve radical cascade difluoromethylation of acrylamides **1** to obtain valuable difluoromethylated oxindoles **3** with good efficiencies. Experimental evidence pointed out a crucial role of the iron catalysis in the reaction. Optimization studies revealed that addition of iodosobenzene pivalate secures the optimal reaction yield. Newly developed protocol is compatible with multiple substrate features, giving access to a wide variety of added-value difluoromethylated products. In addition, the radical mechanism of the given process was proven by radical trapping experiments.



1 2 3

25 examples, up to 86% yield

Scheme 1. Difluoromethylation of *N*-arylacrylamides leading to difluoroethyl-substituted oxindoles

References

[1] Zafrani, Y.; Yeffet, D.; Sod-Moriah, G.; Berliner, A.; Amir, D.; Marciano D.; Gershonov E.; Saphier S. *J. Med. Chem.*, **2017**, *60 (2)*, 797-804.
[2] Li, X.; Song, Q. *Eur. J. Org. Chem.*, **2024**, *27*, e202400423.
[3] Ford, J.; Hopkin, B.; Sap, J. B. I.; Gouverneur, V. *Isr. J. Chem.*, **2023**, *63*, e202300109.
[4] Solomin, V.; Liard, M.; Jubault, P.; Castanheiro, T. *Org. Chem. Front.*, **2025**, *12*, 1467-1473

S_NAr Reactions of Phenol Derivatives with Fluorobenzene

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Diphenyl ether is an important structure due to its widespread occurrence and diverse applications in natural compounds, pharmaceuticals, enzymes, and inhibitors. [1] As a general concept we have explored S_NAr reactions for *N*-, *O*- or *S*-arylations. [2, 3, 4, 5] In this communication we present the synthesis of diphenyl ether from phenols and fluorobenzene derivatives via S_NAr reactions. Various phenol derivatives reacted with the fluorobenzenes under optimized basic conditions, examining the influence of phenol pKa and the steric effects. This approach enables efficient and convenient diphenyl ether synthesis. The methodology was successfully applied to complex phenol-containing natural products, highlighting the potential for application in late-stage modification of bioactive compounds.

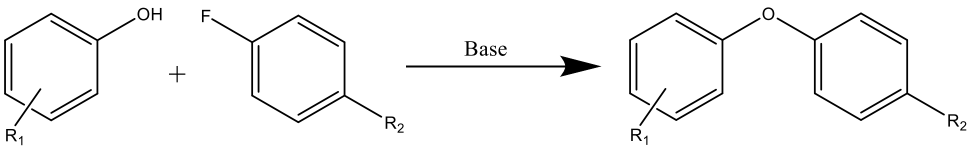

Figure 1. Phenol derivatives with fluorobenzene using S_NAr reaction.

References

[1] Hou J, Zhao W, Huang Z N, et al. *Chemical Biology & Drug Design*, **2015**. *86(2)*: p. 223-231.

[2] Nikitin, S., Lie, Y., Diness, F. *Macromolecular Chemistry and Physics*, **2022**, *223(13)*: 2100484.

[3] Embaby, A. M.; Schoffelen, S.: Kofoed, C.; Meldal, M.; Diness, F. *Angew. Chemie Int. Edition*, **2018**, *57*, 8022-8026

[4] Jacobsen, C. B.; Meldal, M.; Diness, *F. Chemistry - A European Journal*, **2017**, *23*, 846-851

[5] Diness, F.; Fairlie, D. P. *Angew. Chemie Int. Edition*, **2012**, *51*, 012-8016.

Pyridinium-based Fluorosulfonamide Reagents Enabled Photoredox-catalyzed Radical Fluorosulfonamidation.

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Sulfamoyl fluorides, as a crucial building block of SuFEx, have garnered extensive research interest due to their unique properties. However, the direct radical fluorosulfonamidation process for the synthesis of sulfamoyl fluorides has been overlooked. We herein disclosed a practical procedure for constructing a redox-active fluorosulfonamide radical reagent named fluorosulfonyl-N-pyridinium tetrafluoroborate (PNSF) from SO2F2. These reagents can facilitate a range of reactions, including the N-(fluorosulfonyl) sulfonamidation of (hetero)arenes, sequential radical stereoselective fluorosulfonamidation, and 1,2difunctionalization of alkenes.

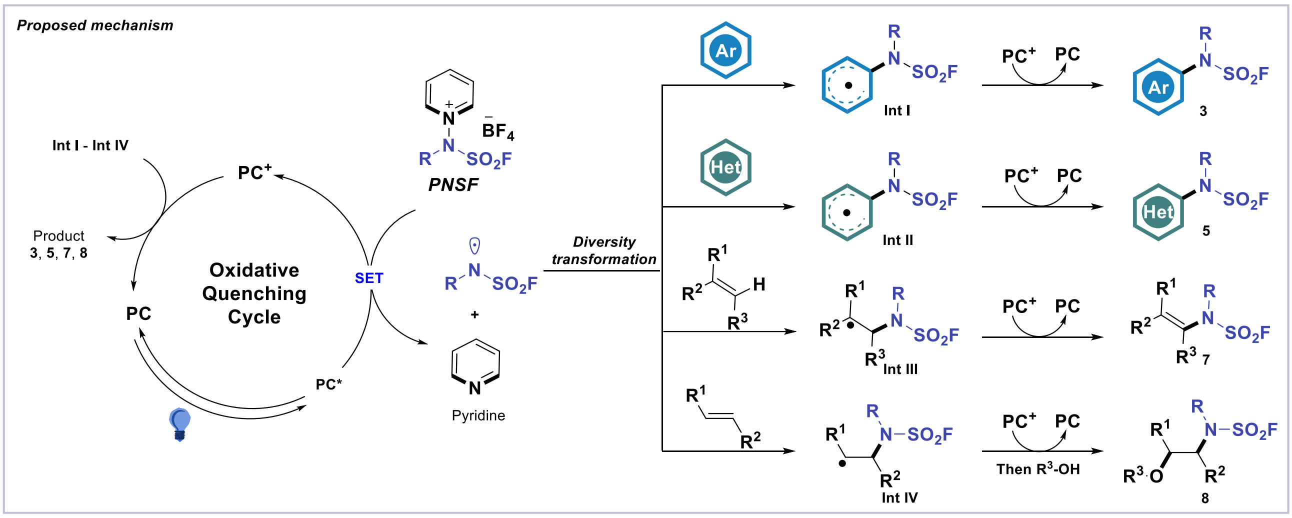

Figure 1. PNSF reagent for radical fluorosulfonamidation of unsaturated hydrocarbons

References

[1] Heyin Li, Xian Zhang, Zhen Wang, Chao Sun, Mengjun Huang, Jing Liu, Yifan Li, Zhenlei Zou, Yi Pan, Weigang Zhang*, Yi Wang*. *Org. Lett.* **2024**, 26, 6714–6719.

[2] Heyin Li, Mengjun Huang, Zhenlei Zou, Zhen Wang, Yifan Li, Chao Sun, Wangzhe Chen, Yi Pan, Weigang Zhang*, Yi Wang*. *Chem. Sci.,* **2023**,14, 13893-13901.

[3] Weigang Zhang, Heyin Li, Xiaojuan Li, Zhenlei Zou, Mengjun Huang, Jiyang Liu, Xiaochen Wang, Shengyang Ni, Yi Pan & Yi Wang*, Nature Communications, **2022**, 13, 3515.

The Reactivity of Tetrafluoro(trifluoromethyl)-λ^6-sulfanyl chloride (CF_3SF_4Cl) with Substituted Alkynes and Reactions of the Adducts Formed.

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In the course of the exploration of the electron withdrawing and lipophilic effects of trifluoromethyl tetrafluoro-λ^6-sulfanyl (CF_3SF_4-) group on reactivity, various CF_3SF_4-substituted olefins have been prepared.[1] The preparation of the crucial reagent trifluoromethyl tetrafluoro-λ^6-sulfanyl chloride (CF_3SF_4Cl) has recently been improved by the using *S*-trifluoromethyl trifluoromethylanesulfonothioate (TTST) to prepare the intermediate trifluoromethyl disulfide.[2] Unfortunately, the typical addition reactions of trifluoromethyl tetrafluoro-λ^6-sulfanyl chloride (CF_3SF_4Cl) are limited by the concurrent addition of chlorine along with the trifluoromethyl tetrafluoro-λ^6-sulfanyl (CF_3SF_4-) group. Excision of the chlorine from the products requires additional transformations. It has been found that the addition of CF_3SF_4Cl) to 2-propynoic acid yields principally 3-CF_3SF_4-2-propenioc acid. As the mechanism behind this addition remains unknown, the influence of solvation on this process and on the yield of the non-chlorinated product will be reported. The utility of alkyl 3-CF_3SF_4-2-propenoates in 1,4-addition, epoxidation and other reactions will be described. In comparison the reactivity of (2-CF_3SF_4-ethynyl) arenes which have been prepared in good yields with electrophiles will be described. Addition reactions to these sterically hindered, unsaturated products under both catalytic and non-catalytic conditions were examined. Studies of the transformations of the addition products are ongoing.

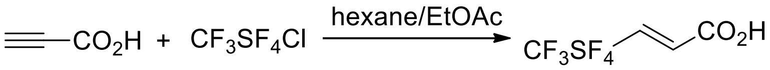

Figure 1. Addition of CF_3SF_4Cl to 2-propynoic acid

References

[1 Ikeda, A.; Capellan, A.; Welch, J. T. *Org. Biomol. Chem.* **2019**, *17* (35), 8079-8082.

[2] Yang Y.; Miraghaee S.; Pace R.; Umemoto T.; Hammond G. B. *Angew. Chem. Int. Ed.* **2023**, 62, e202306095

[3] Popek, L.; Nguyen, T. M.; Blanchard, N.; Cahard, D.; Bizet, V. *Org. Lett.* **2024**, 26, 365–369

The Influence of *N*-(2-(tetrafluoro(trifluoromethyl)-λ^6-sulfanyl)ethyl)((*N*-CF_3SF_4-ethyl) Groups on Peptide Bond Formation and on Amide Bond Conformation.

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Both the pentafluorosulfanyl (SF_5) and tetrafluoro(trifluoromethyl)sulfanyl ((CF_3SF_4) substituents have been shown to influence the secondary structure of heptapeptides when incorporated in the amino acid side chains of the first and fifth amino acids of the heptapeptides.[1, 2] This effect has been attributed to the hydrophobicity and steric demand of the SF_5 and CF_3SF_4 groups. However, preparation of the necessary optically active precursors is challenging. Recently we have found that *N*-CF_3SF_4-ethyl amino acids can be simply and efficiently prepared.[3] The influence of the *N*-CF_3SF_4-ethyl group on amide bond forming reactions will be described as well as the preparation of oligopeptides containing peptoid bonds. The influence of *N*-CF_3SF_4-ethyl group on native chemical ligation processes will also be reported. The effect of the *N*-CF_3SF_4-ethyl group on *cis-trans* amide bond ratios will be discussed.

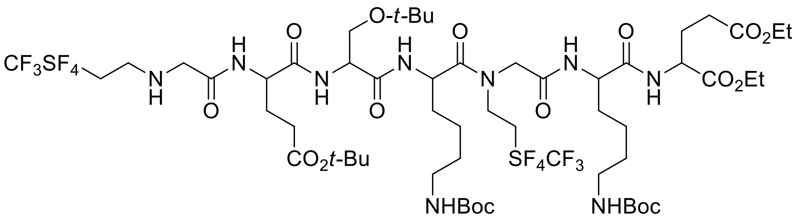

Figure 1. Heptapeptide containing an *N*-CF_3SF_4 ethyl peptoid bond.

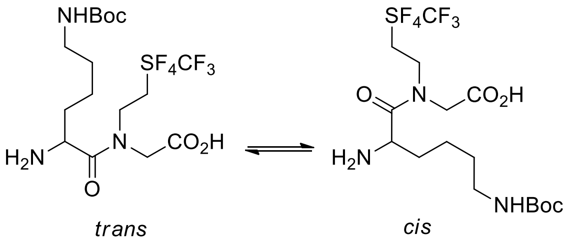

Figure 2. *Cis-trans* isomerization

References

[1] Ikeda, A.; Capellan, A.; Welch, J. T. *Org. Biomol. Chem.* **2019**, *17* (35), 8079-8082.
[2] Lim, D. S.; Lin, J.-H.; Welch, J. T. *Eur. J. Org. Chem.* **2012**, *2012* (21), 3946-3954.
[3] Deng, M.; Wilde, M.; Welch, J. T. *J. Org. Chem.* **2023**, *88* (22), 15639-15646..

The Application of Sulfur Hexafluoride in Synthetic Chemistry for Pentafluorosulfanylation

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The interest of SF$_5$-funcionalized molecules is increasing in the last decade for their application in agrochemistry, medical chemistry and optoelectronics.[1,2] The synthetic access to those compounds is mostly limited by the utilization of toxic compounds like SF$_5$Br/Cl. [3] Wagenknecht *et al.* used sulfur hexafluoride to obtain pentafluorosulfanylated structures, using 1,1-Diphenylethylene and α-Methylstyrene. We present the further application of this method in order to obtain novel interesting SF$_5$-functonalized molecules.

References

[1] M. F. Sowaileh, R. A. Hazlitt, D. A. Colby, *ChemMedChem* **2017**, *12*, 1481–1490.
[2] J. G. Kim, O.-Y. Kang, S. M. Kim, G. Issabayeva, I. S. Oh, Y. Lee, W. H. Lee, H. J. Lim, S. J. Park, *Molecules* **2020**, *25*, 5536.
[3] P. R. Savoie, J. T. Welch, *Chem. Rev.* **2015**, *115*, 2, 1130–1190.
[4] D. Rombach, H.-A. Wagenknecht, *ChemCatChem* **2018**, *10*, 2955-2961.

Expanding the Chemical Space of Pentafluorosulfanyl-containing Compounds

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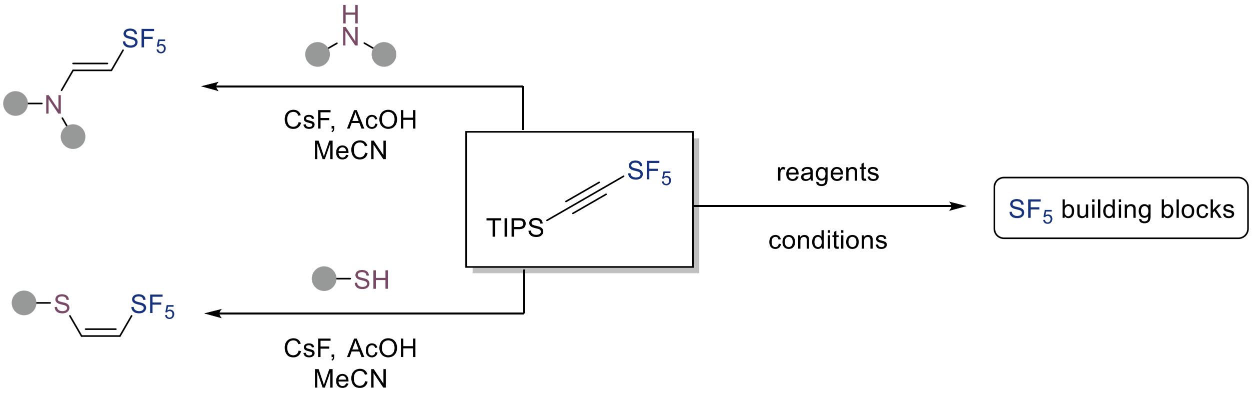
Compounds with pentafluorosulfanyl (SF_5) motif have unique electronic structures. They have shown unique physiological properties in lipophilicity, pKa, metabolic stability, and have emerged to be useful candidates for pharmaceutical, agrochemical and material industries. SF_5-containing compounds have also been suggested to be benign alternatives to per- and poly-fluoroalkyl compounds, which have caused potential hazards to the environment and health due to the poor bio-degradability and prolonged lifetime. However, synthetic access to a range of aliphatic and vinylated SF_5 scaffolds still remains a major challenge, due to reliance on toxic reagents and lack of mild and efficient reaction protocols. Recently, we became interested in the exploitation of prefunctionalised reagents to grant access to new classes of fundamental building blocks by downstream functionalisation.

Herein, we report novel transformations based on a simple silyl-protected SF_5-containing building block as the starting material to access a variety of novel classes of building blocks. We previously reported hydroamination and hydrothiolation reactions [1,2], employing mild conditions with good to excellent product yields. The newly accessed classes of molecules have shown remarkable chemical stability, and multiple handles on the molecules enable them to be further functionalised easily by employing simple procedures to expand the chemical space and synthetic utility of SF_5-containing compounds.



Scheme 1. Access to various SF_5 building blocks with a single substrate and beach-top conditions

References

[1] J. O. Wenzel, F. Jester, A. Togni, D. Rombach, *Chem. Eur. J.* **2024**, 30, e202304015 (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-brg1w).

[2] H. Kucher, J. O. Wenzel, D. Rombach, *ChemPlusChem* **2024**, 89, e202400168. (*ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-01jhn).

Novel Hexafluorosulfur Activation Utilizing an Organic Photoredox Catalyst

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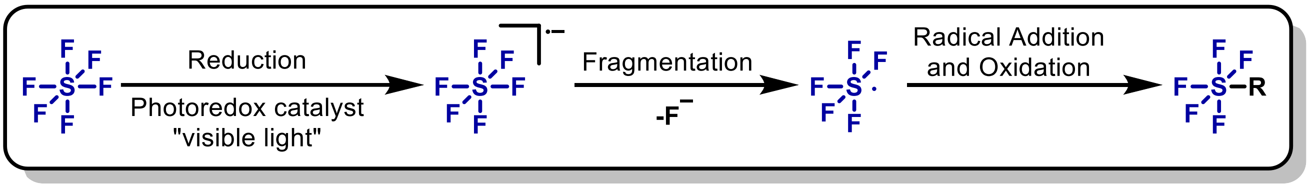
Pentafluorosulfanyl substituted compounds showcase a unique and novel utility in modern fluorine chemistry. In recent years the environmental issues of compounds employing fluorocarbon bonds have been becoming more apparent.[1] Therefore, the search for moieties with similar properties and their respective chemical transformation is essential. The pentafluorosulfanyl group is a prime candidate for such an area of application due to its unique electronic structure and steric demand.[2] Conclusively, we present the generation of high value chemicals bearing the pentafluorosulfanyl group, by reducing the inert and non-toxic sulfur hexafluoride via photoredox catalysis employing visible light.[3,4]



Scheme 1. General proposed mechanism of the photocatalytic reductive activation and addition of sulfur hexafluoride to yield a variety of high value pentafluorosulfanyl structures.

References

[1] M. Bonato; F. Corrà; M. Bellio; L. Guidolin; L. Tallandini; P. Irato; G. Santovito *Int. J. Environ. Res. Public Health*, **2020**, *17* (*21*), 8020.

[2] R. Kordnezhadian; B. Li, A. Zogu; J. Demaerel; W. M. De Borggraeve; E. Ismalaj *Chem. Eur. J.,* **2022**, *28*, e202201491.

[3] D. Rombach; H. Wagenknecht *ChemCatChem,* **2018**, *10*, 2955 – 2961.

[4] D. Rombach; H. Wagenknecht *Angew. Chem. Int. Ed.,* **2020**, *59*, 300 –303.

Investigating DNA Binding of All-*cis* Pentafluorocyclohexanes using FRET.

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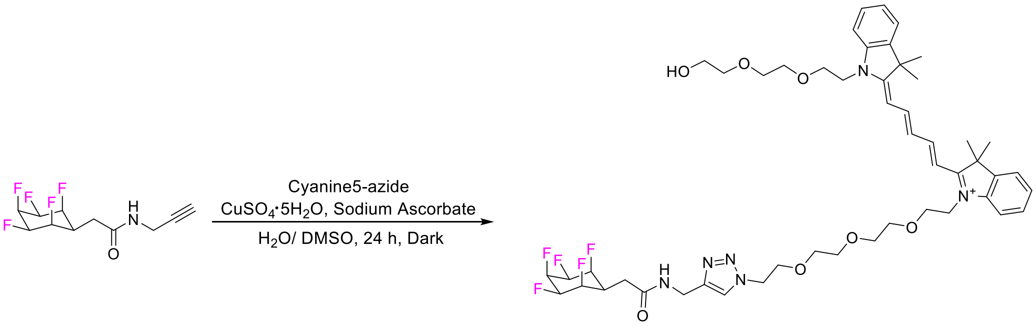
All-cis-1,2,3,4,5,6-hexafluorocyclohexane, first synthesised in St Andrews, has the highest molecular dipole moment of all aliphatic compounds[1] due to the facially polarised "Janus-face" motif present in this molecule. Recent developments in the synthesis of poly-fluorinated "Janus-face" molecules[2] has allowed for the efficient synthesis of a range of compounds containing this motif, enabling incorporation as a building block into larger molecular structures. A diversity of areas are being explored exploiting the unusual properties of this motif, including in supramolecular assemblies and as a motif in medicinal chemistry.

This work reports the synthesis of cyanine-dye structures containing the pentafluoro "Janus-face" motif and the subsequent investigation of the binding properties of this motif with single-stranded and double-stranded DNA. CuAAC-enabled "click" chemistry provides access to target molecules.



1 2

Scheme 1. CuAAC click synthesis of Cy5 containing FRET-active DNA binding probe.

Experiments including single-molecule microscopy and fluorimetry have been undertaken to examine DNA binding behaviour. Differences in behaviour between double-stranded and single-stranded DNA has been identified, with a preference for binding with double-stranded DNA observed.

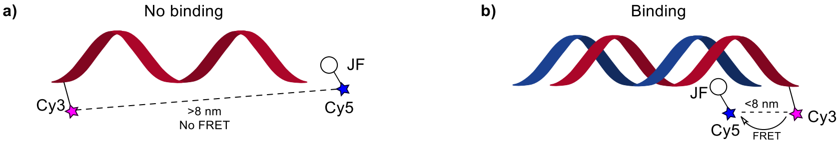


Figure 1. a) No FRET induction **b)** DNA Binding induced FRET utilising JF-Cy5 structure **2**

References

[1] Keddie, N. S.; Slawin, A. M. Z.; Lebl, T.; Philp, D.; O'Hagan, D., *Nat. Chem.*, **2015**, 7, 483-488.
[2] Clark, J. L.; Neyyappadath, R. M.; Yu, C.; Slawin, A. M. Z.; Cordes, D. B.; O'Hagan, D., *Chem. Eur. J.,* **2021**, 27, 16000

Photo-catalytic Synthesis of Fluorinated Superacidic Carbon Acids

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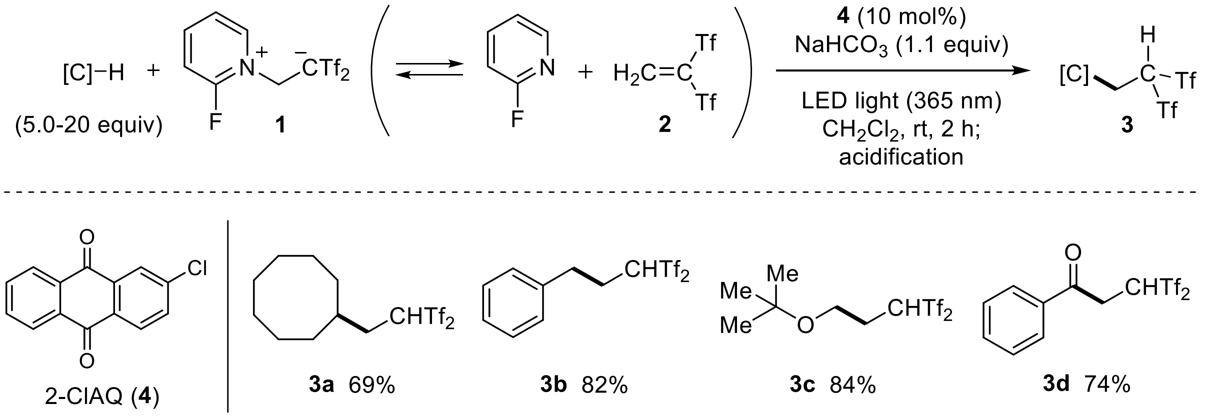
Organic molecules bearing bis(triflyl)methyl group(s) exhibit comparable Brønsted acidity to sulfuric acid and related sulfonic acid molecules.[1] Their conjugate bases are also isolable and stable carbanions.[2] To prepare such superacidic molecules and stable carbanion-containing salts, we successfully developed an easy-to-handle reagent **1** for the in-situ generation of $Tf_2C{=}CH_2$ **2** (Scheme 1). For example, the treatment of several neutral nucleophiles, such as electron-rich arenes, alkenes, and active methylenes, with this reagent caused clean formations of Tf_2CH-based acid molecules through electrophilic addition of $Tf_2C{=}CH_2$. In this context, we recently examined the reaction of photochemically generated carbon-centred radicals with the in-situ generated $Tf_2{=}CH_2$. Fortunately, the desired C-H functionalisation reaction of hydrocarbons or aldehydes with $Tf_2C{=}CH_2$ smoothly proceeded under photo-HAT (hydrogen atom transfer) conditions[3] to give the corresponding carbon acids **3**. The details will be presented in my poster.



Scheme 1. The C-H 1,1-Bis(triflyl)ethylation reactions under photo-HAT conditions.

References

[1] For a review, see: H. Yanai, T. Taguchi, *J. Fluorine Chem*. **2015**, *174*, 108. [2] For a review, see: H. Yanai, *Chem. Rec.* **2023**, *23*, e202300076. [3] S. Kamijo et al. *Org. Lett*. **2016**, *18*, 4912.

Synthesis and Properties of Selectively Fluorinated *tert*-Leucine Derivatives

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The *tert*-butyl group is known for being a sterically demanding, non-polar substituent. However, it is underrepresented in pharmaceuticals due to its hydrophobic nature and metabolic instability due to its high LogP.[1] Sequential replacement of methyl groups of *tert*-butylbenzene for fluoromethyl groups (CH_2F) has been shown to significantly impact LogP, as well as the overall metabolic stability of the compounds.[2]

Recent work has described synthesis of both aryl(β,β',β''-trifluoro)-*tert*-butyl (TFTB) compounds **1**,[2] as well as (γ,γ',γ''-trifluoro)neopentyl aryl ethers **2**.[3] This work is focussed on generating selectively fluorinated *tert*-leucine derivatives, assessing their properties, and incorporation into bioactive molecules.

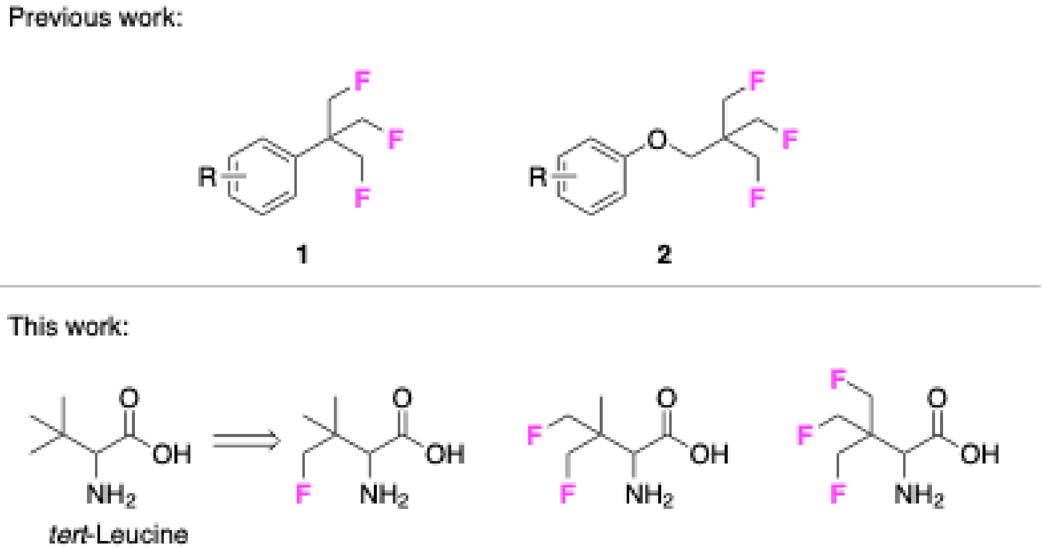

Figure 1. Previous work involving the TFTB group and current work exploring the amino acid derivatives.

References

[1] Westphal, M. V.; Wolfstäder, B. T.; Plancher, J-M; Gatfield, J.; Carreira, E. M.; *ChemMedChem*, **2015**, *10(3)*, 461-469

[2] Dobson, L. S.; Zhang, Q.; McKay, B. A.; Oke, O.; Isanbor, C.; Faheem Khan, M.; Piscelli, B. A.; Cordes, D. B.; Cormanich, R. A.; Murphy, C. D.; O'Hagan, D.; *Org. Lett.*, **2023**, *25(37)*, 6802-6807.

[3] Tarui, A.; Piscelli, B. A.; Al-Maharik, N.; Stewart, J. M.; Niemcová, P.; Cordes, D. B.; McKay, A. P.; Murphy, C. D.; Cormanich, R. A.; O'Hagan, D.; *Chem. Eur. J.*, **2024**, *30(57)*, e202402532.

Unlocking the Pentafluorosulfanylation Reactivity of SF_6 by Photoredox Catalysis

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The pentafluorosulfanyl group is a precious addition to the toolbox of medicinal chemistry, agrochemists and material scientists and might provide alternatives to PFAS based materials. However, the challenging synthesis of SF_5-containing building blocks hampers rapid progress in the understanding and application of pentafluorosulfanylated materials. Therefore, the development of new strategies to avoid the use of hazardous reagents is a key challenge in modern organofluorine chemistry. We recently became interested to access SF_5-containing materials by unlocking a new mode of reactivity of sulfur hexafluoride.
The specific activation of only one single fluoride atom of the molecule, turning it into a precious pentafluorosulfanylation reagent, was disputed in the past. Recently, we were able to decipher this new type of reactivity in proof-of-principle studies enabled by photoredox catalysis. The insights of a proof-of-concept study on the addition of SF_6 to styrenes could be exploited to develop the first alkoxypentafluorosulfanylation protocol and ultimately led to the development of a three-component cascade reaction granting access to pentafluorosulfanylated oxaheterocycles by 5,6 or 7-exo-dig cyclization in a single reaction step.

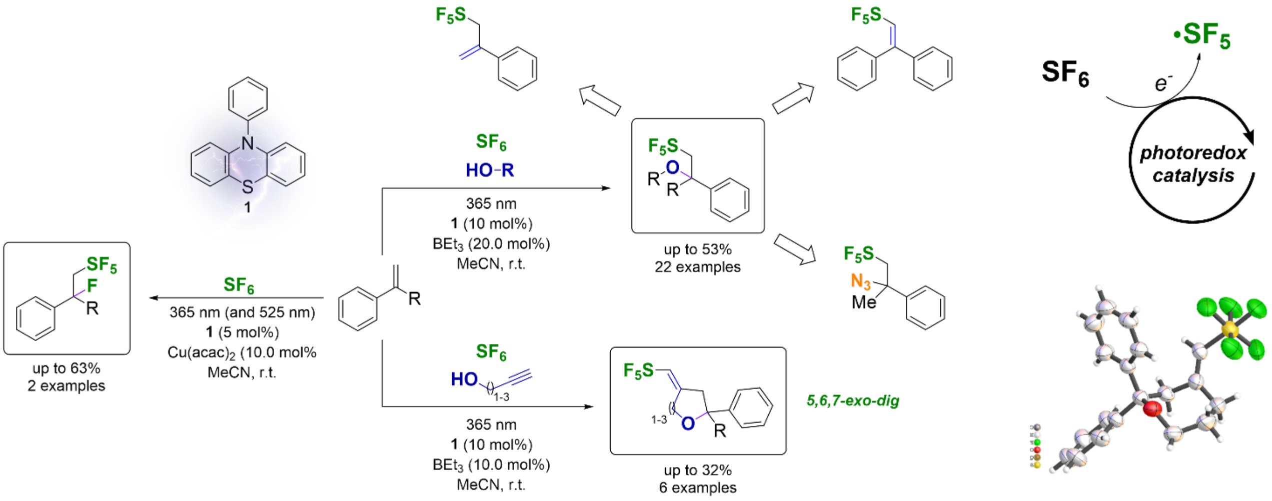

Figure 1. Photoredox catalytic SF_6 activation for pentafluorosulfanylation chemistry.

References

[1] D. Rombach, H.-A. Wagenknecht*, *ChemCatChem* **2018**, 10, 2955.
[2] D. Rombach, H.-A. Wagenknecht*, *Angew. Chem. Int. Ed.* **2020**, *59*, 300.
[3] D. Rombach*, B. Birenheide, H.-A. Wagenknecht*, *Chem. Eur. J.* **2021**, 27, 8088.

Synthesis of α,α-Difluoro-β-thiocarboxylates For a Cystatin-Free Chemical Ligation

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Native chemical ligation (NCL) is a peptide-fusion reaction for an access to medium-sized peptides. Generally, this process proceeds via *S*-to-*N* acyl transfer using the thiol of cysteine residues (Fig. 1). However, cysteines are present in only 1.7% of common peptides, and therefore peptide ligation by this method often involves the introduction of undesired cysteine residues. On the other hand, synthetic examples using *C*-terminal thiocarboxylates as a cysteine-free ligation methodology have been reported.[1] Therefore, the construction of highly active thiocarboxylates is a key framework for a widespread peptide ligation. In this context, we have achieved the synthesis of fluorinated dipeptides by the reaction of difluoro-β-lactams with *N*-nucleophiles in 2,2,2-trifluoroethanol (TFE) as a route to construct β-amino acid units,[2] and the synthesis of difluoro-β-amino esters by the reaction of *O*-nucleophiles (Scheme 1a). Herein, we will report the conversion toward α,α-difluoro-β-thiocarboxylates by the reaction of difluoro-β-lactam (**1**) with *S*-nucleophiles.
The reaction of **1** with dodecanethiol (**2a**) provided difluoro-β-thiocarboxylate (**3**) in good yield (Scheme 1b). Modification of solvent system from TFE to DMF worked well, in which a homogeneous solution gave good conversions of **1** to **3**. In this report, we will discuss the synthesis of **3** from various *S*-nucleophiles.

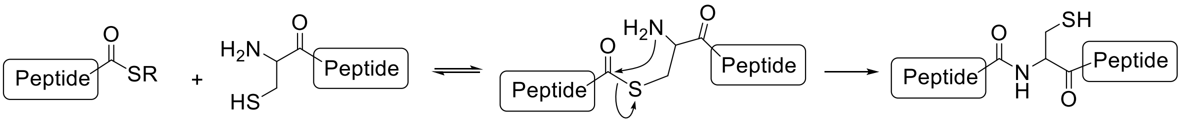
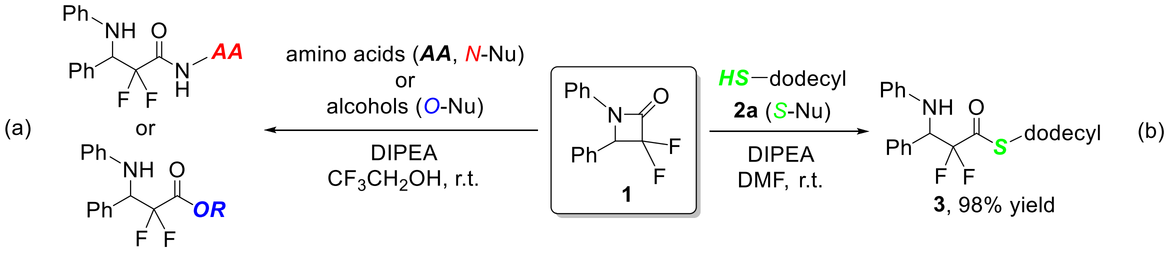


Figure 1. Classical Native Chemical Ligation (NCH) for a linkage of peptides.



Scheme 1. a) Previous work, b) Nucleophilic ring-opening reaction of **1** with *S*-Nu species.

References

[1] a) H. Chen, X. Hong, et al., *Green Chem.*, **2011**, *13*, 2723-2726; b) J. Duan, X. Hang, et al., *J. Org. Chem.*, **2013**, *78*, 7013-7022.
[2] A. Tarui, M. Omote, et al., *Synthesis*, **2020**, *52*, 3667-3666.

Room Temperature Ionic Liquids – Advanced Reaction Media for Organic Syntheses with Highly Reactive Chemicals – Let's Make Fluorination Safer

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Room temperature ionic liquids (RTILs) consist of weakly coordinated organic cations and weakly coordinating anions primarily containing fluorine. Room temperature ionic liquids typically reveal unique properties: high thermal and electrochemical stability, electrical conductivity, and the ability to dissolve many organic and inorganic substances. Some RTILs have a relatively low viscosity – a crucial parameter for practical applications. In addition, ionic liquids are non-volatile and non-inflammable, in general. This unique combination of properties makes RTILs valuable materials for applications for various chemical processes. However, a comparably high price limits the use of these ionic liquids, and only in some cases RTILs are real alternatives to common organic solvents. Recently we have evaluated ionic liquids as reaction media in organic synthesis with highly reactive substances such as F_2, Br_2, SF_4, $POCl_3$, NaN_3, N-F reagents, *etc.*[1-11] Here, ionic liquids lead to a safer handling and less dangerous reaction conditions. Several examples for reactions of these reagents in ionic liquids will be presented. Moreover, the use of ionic liquids as reaction media enables a simple isolation of volatile fluorinated compounds especially as they tend to form azeotropic mixtures with conventional organic solvents. The synthesis of some fluorinated substances containing $(CF_3)_2N$-substituents in ionic liquids will be presented.[12]

References

[1] Hirschberg, M.E.; Ignat'ev, N.V.; Wenda, A.; Willner, H. *J. Fluorine Chem.*, **2012**, *137*, 50-53.
[2] Zavozin, A.G.; Kravchenko, N.E.; Ignat'ev, N.V.; Zlotin, S.G. *Tetrahedron Lett.*, **2010**, *51*, 545-547.
[3] Zavozin, A.V.; Ignat'ev, N.V.; Schulte, M.; Zlotin, S.G. *Tetrahedron*, **2013**, *69*, 6975-6980.
[4] Serguchev, Y.A.; Lourie, L.F.; Ponomarenko, M.V.; Rusanov, E.B.; Ignat'ev, N.V. *Tetrahedron Lett.*, **2011**, *52*, 5166-5169.
[5] Lourie, L.F.; Serguchev, Y.A.; Ponomarenko, M.V.; Rusanov, E.B.; Vovk, M.V.; Ignat'ev, N.V. *Tetrahedron*, **2013**, *69*, 833-838.
[6] Epishina, M.A.; Kulikov, A.S.; Ignat'ev, N.V.; Schulte, M.; Makhova, N.N. *Mendeleev Commun*., **2010**, *20 (6)*, 335-336.
[7] Sheremetev, A.B.; Alexandrova, N.S.; Ignat'ev, N.V.; Schulte, M. *Mendeleev Commun*., **2012**, *22 (2)*, 95-97.
[8] Epishina, M.A.; Kulikov, A.S.; Ignat'ev, N.V.; Schulte, M.; Makhova, N.N. *Mendeleev Commun*., **2011**, *21 (6)*, 334-336.
[9] Epishina, M.A.; Kulikov, A.S.; Struchkova, M.I.; Ignat'ev, N.V.; Schulte, M.; Makhova, N.N.; *Mendeleev Commun*., **2012**, *22 (5)*, 267-269.
[10] Epishina, M.A.; Kulikov, A.S.; Ignat'ev, N.V.; Schulte, M.; Machova. N.N. *Mendeleev Commun*., **2015**, *25 (1)*, 41-43.
[11] Ignat'ev, N.V.; Schulte, M.; Zlotin, S.G.; Makhova, N.N.; Sheremetev, A.B.; Serguchev, Y.A.; Shermolovich Y.G., X. German-Russian-Ukrainian Symposium on Fluorine Chemistry, Berlin, November 26-28, 2014; Book of Abstracts, p. 21.
[12] Breitenstein C.; Ignat'ev N.; Frank W. *J. Fluorine Chem.* **2018**, *210,* 166-177.

Application of CF_3-Nitrile Imines in the Synthesis of Unsymmetrical *N*',*N*'-Trifluoroacetohydrazides

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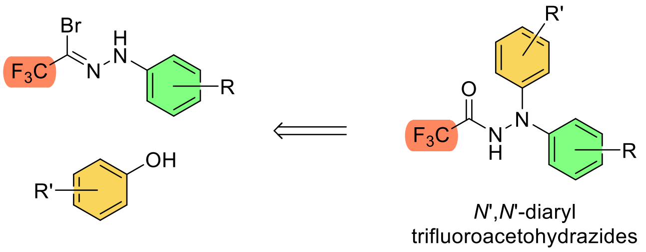
Although *N*',*N*'-diaryl-acylhydrazide group occurs rarely in natural products, synthetic hydrazides of that type has been demonstrated as privileged structural motif of numerous pharmaceuticals and agrochemicals.[1] In addition, the mentioned hydrazides are convenient substrates for preparation of more complex heterocyclic systems including indazoles and benzo-1,2,4-triazines.[2] However, despite well-documented positive effects caused by introduction of fluoroalkyl groups into organic systems, fluorinated acylhydrazides are known to a limited extent. It is due to remarkable limitations of the classical synthetic methods comprising condensation of carboxylic acids (or derivatives) with appropriate hydrazines, catalytic Ullmann type *N*-arylations of readily available *N*-aryl-acylhydrazides, and azaphilic additions to azo compounds.[1-3] In continuation of our study on fluorinated 1,3-dipolar reagents,[4] here we report on efficient synthesis of unsymmetrical *N*',*N*'-diaryl-trifluoroacetohydrazides based on a two-step protocol comprising trapping the *in situ* generated CF_3-nitrile imine with phenolate followed by Smiles rearrangement of the first formed hydrazonyl ester.



Scheme 1. Structures of target unsymmetrical hydrazides and key starting materials.

References

[1] (a) L. Deng, et al., *Org. Chem. Front.* **2024**, *11*, 1132; X. Han, et al., *J. Med. Chem.* **2016**, *59*, 2139; (c) V.N. Barinova, et al., *Pharm. Chem. J.* **1988**, *22*, 851.
[2] (a) J-Q. Zhang, et al., *Org. Biomol. Chem.* **2015**, *13*, 2055; (b) E.B. Elkaeed, J. An, A.M. Beauchemin, *J. Org. Chem.* **2017**, *82*, 9890.
[3] J. Yang, et al., *Org. Lett.* **2024**, *26*, 498; A.A. Berezin, et al., *J. Org. Chem.* **2014**, *79*, 314.
[4] (a) A. Kowalczyk, et al., *Org. Lett.* **2022**, *24*, 2499; (b) K. Świątek, et al., *Org. Lett.* **2023**, *25*, 4462; (c) G. Utecht-Jarzyńska, et al., *RSC Mechanochemistry* **2025**, *2*, 79.

Synthetic Strategies Leveraging Fluoride-Enabled Reactivity and Selectivity

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The high strength and polarity of C–F bonds give rise to many of the desirable properties of fluorinated pharmaceuticals, agrochemicals, polymers, and functional materials. However, these defining characteristics also make fluorinated compounds difficult to functionalize, often requiring the use of specialized catalysts or reagents to effect C–F bond cleavage under mild conditions. Notwithstanding these inherent challenges, the use of C–F bond electrophiles can offer distinct synthetic advantages, such as enabling unique reactivity, chemoselectivity, and stereoselectivity when paired with an appropriate fluorophilic catalyst or reagent.

Over the past few years, my group has explored the preparation and synthetic utility of carbamoyl fluorides, an emerging class of electrophiles that can provide entry to medicinally important amides and *N*-heterocycles through C–F bond functionalization. Although the chemistry of the analogous carbamoyl chlorides has been extensively developed, synthetic applications of carbamoyl fluorides remain underexplored. In this presentation, I will discuss the application of carbamoyl fluorides in diverse synthetic transformations, such as cross-coupling, nucleophilic substitution, and halide recycling. Mechanistic studies involving reaction kinetics, intermediate isolation, and DFT calculations will be presented to support the role of fluoride in promoting reactivity and/or selectivity in the developed transformations.

References

[1] Cadwallader, D.; Tiburcio, T. R.; Cieszynski, G. A.; Le, C.M. *J. Org. Chem.* **2022**, *87*, 11457–11468.

[2] McKnight, E. A.; Arora, R.; Pradhan, E.; Fujisato, Y.; Ajayi, A.; Lautens, M.; Zeng, T.; Le, C. M. *J. Am. Chem. Soc.* **2023**, *145*, 11012–11018.

[3] Cadwallader, D.; Shevchuk, D.; Tiburcio, T. R.; Le, C.M. *Org. Lett.* **2023**, *25*, 7369–7373.

[4] Jabbarpoor, M.; LeBlanc, J.; Chen, Z.; Cadwallader, D.; Le, C. M. *Chem. Commun.*, **2024**, *60*, 8700–8703.

Bicyclo[1.1.1]pentanes with Fluoro and Fluoroalkyl Substituents: Redox-Active Esters and Their Reactivity

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Bicyclo[1.1.1]pentanes (BCPs) are being investigated as new building blocks to replace a common structural unit: arenes. While BCPs can be used as bioisosteres of planar arenes, they possess a unique cage-like shape made of *sp*^{3}-hybridized carbons, and this has been found to improve the pharmacological profile of drugs.

This work focuses on the synthesis of fluorinated BCP redox-active esters (RAEs) and their reactivity towards carbon-element bond formation. The goal is to synthesize building blocks incorporating bridgehead-fluorinated or -fluoroalkylated BCPs. This is driven by the proven enhancements that fluorinated fragments can have on pharmaceuticals, such as decreasing toxicity and increasing potency. Imide-based RAEs are positioned on the other bridgehead-carbon of the BCP and provide multiple avenues to make carbon-element bonds, specifically through the formation of a radical on the bridgehead of BCPs after decarboxylation of the RAE.

The current route that is being explored investigates reacting the fluorinated or fluoroalkylated BCP-derived RAEs in Giese radical addition reactions. The goal of this route is to scope the reactivity of a few fluorinated building blocks with a selection of Michael acceptors with diverse structural properties.

Scheme 1. General Strategy

Development of Perfluoro alkoxylation Reagents and Synthesis of Perfluoroalkyl Ethers

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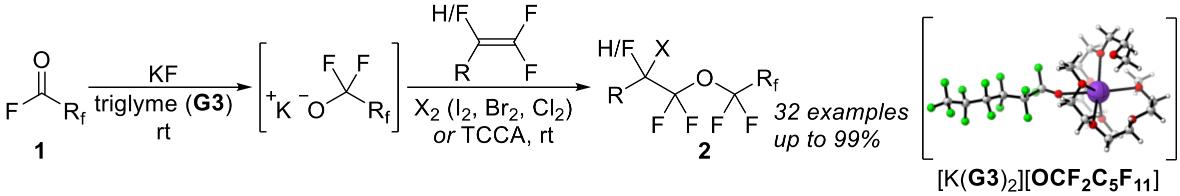
Perfluoroalkyl ether (R–O–Rf) compounds are extensively utilized as pharmaceuticals, agrochemicals, and functional materials. The synthesis of R–O–Rf using perfluoroalkoxides (−ORf) is hindered by low nucleophilicity and stability, leading to decomposition into acyl fluorides through fluoride ion elimination. Therefore, stabilizing −ORf and enhancing its reactivity are critical issues. Recently, the development of OCF3 reagents, precursors for trifluoromethoxide (−OCF3) and trifluoromethoxy radicals (•OCF3), has been frequently reported (Scheme 1). Previously reported OCF3 reagents can be synthesized by the action of Togni reagents or Umemoto reagents on sulfonic acids or N-hydroxylamines. However, long-chain CnF2n−1−Togni reagents are less accessible, hindering the development of long-chain ORf reagents. Therefore, developing ORf reagents using more affordable and user-friendly fluoroalkyl sources is crucial for cost reduction of OCF3 reagents and the development of long-chain ORf reagents.

Our laboratory previously reported that KCF3, prepared from HCF3 and tBuOK, is relatively stable in Glyme solvent and can be used as a trifluoromethylating agent [1]. Based on the hypothesis that KORf could also be stabilized using Glyme solvents, the perfluoroalkoxylation reaction of fluoroolefins was investigated. By exploring various reaction conditions, it was found that the halo-perfluoroalkoxylation reaction proceeds under ambient conditions in triglyme solvent, using an alkoxide derived from perfluoroacyl fluoride 1 and KF, in the presence of halogenating agents such as iodine, resulting in gem–difluoroolefins (Scheme 1) [2].

Moreover, the radical fluoroalkylation of N-hydroxylamines and the development of N−ORf-type reagents, the radical OC2F5 functionalization of aromatic C–H bonds using N−OC2F5 reagents, and the nucleophilic ORf functionalization of haloalkyls using N−ORf-type reagents were also accomplished and will be reported here.



Scheme 1.

References

[1]T. Saito, J. Wang, T. Tokunaga, S. Tsuzuki, N. Shibata, *Sci Rep*, **2018**, *8*, 11501.
[2]K.Kawai, Y. Kato, T. Araki, S. Ikawa, M. Usui, N. Hoshiya, Y. Kishikawa, J. Escorihuela, N. Shibata, *Chem. Sci.*, **2024**, *15*, 9574.

Highly Selective Synthesis of Regio- and Stereoisomers of Fluoroalkylated 1,3-enynes by Optimal Use of Catalyst

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1,3-Enynes are not only structural motifs often found in the skeleton of natural products, but also key synthetic units that can be chemically transformed into various types of substances. Therefore, the development of a simple and efficient synthetic method is highly desired.

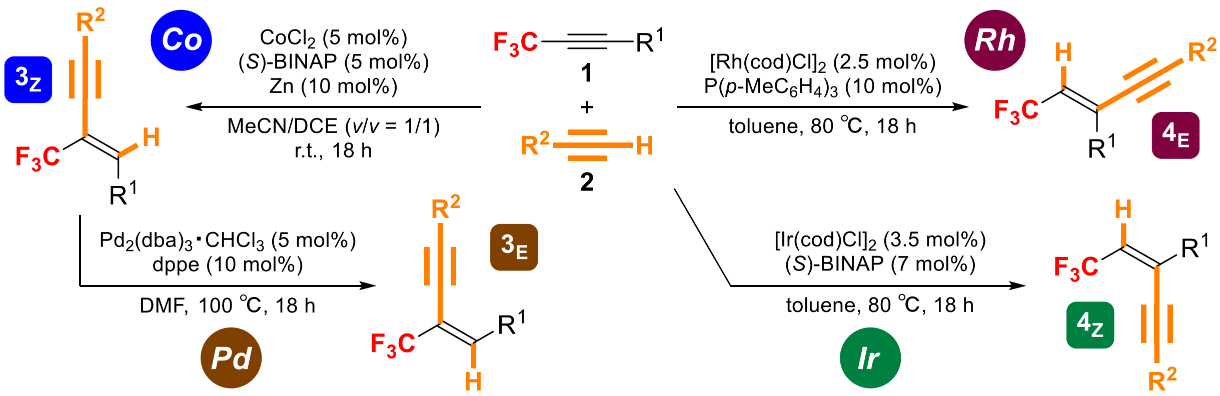
Fluorine-containing 1,3-enynes, in which a fluoroalkyl group is incorporated into 1,3-enynes, are also expected to exhibit interesting properties, such as physiological properties or chemical reactivities due to the unique characteristics of a fluorine atom. However, most of the synthetic methods reported so far are mainly based on the Sonogashira cross-coupling reaction using vinyl halides and terminal alkynes, and no methods have been established that can freely and precisely control both regio- and stereochemistry.

In this study, the authors succeeded in the selective synthesis of fluoroalkylated 1,3-enynes, including their regio- and stereoisomers, *via* the transition metal-catalyzed hydroalkynylation of terminal alkynes to fluoroalkylated alkynes.

Specifically, treatment of fluoroalkylated alkynes **1** with 1.1 equiv. of terminal alkynes **2** in the presence of 5 mol% each of $CoCl_2$ and (*S*)-BINAP, and 10 mol% of zinc in MeCN/$Cl(CH_2)_2Cl$ (*v*/*v* = 1/1) at room temperature for 18 h gave the *Z*-isomer of 1,3-enyne ($\mathbf{3}_{Z}$) with high regio- and stereoselectivity, where the alkynyl group was attached with the carbon having the fluoroalkyl group (**Scheme 1**, *Co*). Furthermore, when the obtained $\mathbf{3}_{Z}$ was treated with 5 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$ and 10 mol% of dppe, an isomerization reaction took place smoothly to give the *E*-isomer ($\mathbf{3}_{E}$), the stereoisomer of $\mathbf{3}_{Z}$, exclusively (**Scheme 1**, *Pd*).

On the other hand, when 2.5 mol% of $[Rh(cod)Cl]_2$ and 10 mol% of $P(p\text{-}MeC_6H_4)_3$ was employed for the reaction of **1** with 1.3 equiv. of **2** in toluene, the *E*-isomer of 1,3-enyne ($\mathbf{4}_{E}$), the regioisomer of $\mathbf{3}_{Z}$ which has the alkynyl group on the carbon bearing R^1 substituent, was obtained in high yield (**Scheme 1**, *Rh*).

Additionally, when 3.5 mol% of $[Ir(cod)Cl]_2$ and 7 mol% of (*S*)-BINAP was used instead of rhodium catalyst, $\mathbf{4}_{Z}$ (the stereoisomer of $\mathbf{4}_{E}$) was selectiv



Scheme 1. Highly selective synthesis of fluoroalkylated 1,3-enyne isomers.

Stereo- and Regioselective Vicinal Fluorosulfonyl-borylation of Unsaturated Hydrocarbons

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The sulfur (VI) fluoride exchange (SuFEx) chemistry as the next-generation click reaction, which rely on the unique reactivity-stability balance of high valent organosulfur, has attracted extensive research interest. The synthetic versatility of the bifunctional handles containing fluorosulfonyl group presents great synthetic value and opportunity for drug discovery. However, the direct fluorosulfonyl-borylation process remains unexplored and challenging due to the system incompatibility and limited synthetic strategies. Herein, we have developed a sequential radical difunctionalization strategy for the highly efficient stereoselective synthesis of vicinal fluorosulfonyl borides with an integrated redox-active SO2F radical reagent. The vicinal fluorosulfonyl borides (VFSB) as orthogonal synthons have been subjected to a range of convenient transformations via the cleavage of C-B bond and S(VI)-F bond, including halogenation, Suzuki coupling, hydrogenation and SuFEX click reaction, which demonstrates great potentials of the vicinal fluorosulfonyl borides (VFSB) moiety in skeleton linkage and drug modification.

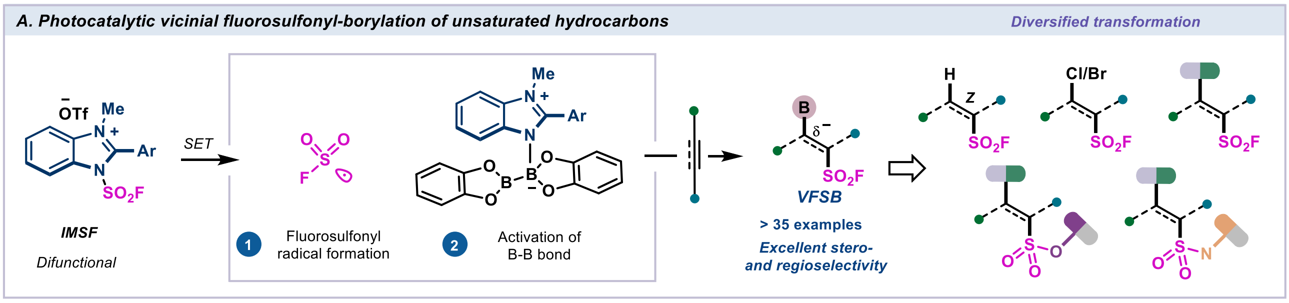

Figure 1. Photocatalytic vicinial fluorosulfonyl-borylation of unsaturated hydrocarbons.

References

[1] Heyin Li, Xian Zhang, Zhen Wang, Chao Sun, Mengjun Huang, Jing Liu, Yifan Li, Zhenlei Zou, Yi Pan, Weigang Zhang*, Yi Wang*. *Org. Lett*. **2024**, *26*, 6714–6719.

[2] Weigang Zhang, Heyin Li, Xiaojuan Li, Zhenlei Zou, Mengjun Huang, Jiyang Liu, Xiaochen Wang, Shengyang Ni, Yi Pan & Yi Wang*, *Nat. Commun*, **2022,** *13*, 3515.

[3] Heyin Li, Mengjun Huang, Zhenlei Zou, Zhen Wang, Yifan Li, Chao Sun, Wangzhe Chen, Yi Pan, Weigang Zhang*, Yi Wang*. *Chem. Sci*, **2023**, *14*, 13893-13901.

Desulfurative Fluorination of Alkyl Phenyl Sulfides

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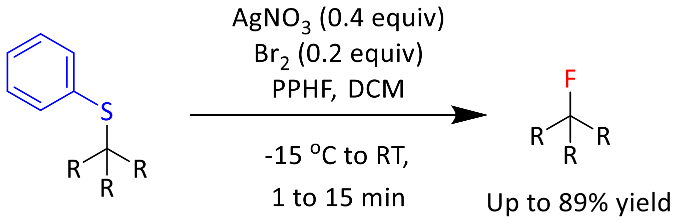
Fluorination of sp^3 carbons is an important transformation in medicinal and synthetic organic chemistry, allowing the manipulation of pharmacokinetic and pharmacodynamic properties of drug candidates, along with having applications in medical imaging through ^{18}F radiolabeling.[1]
Previous work in the Adamo group developed a suite of desulfurative halogenation methodologies achieving high yields and enantiospecificities.[2,3] Building on this work, and prior advancements in desulfurative fluorinations,[4] we present a novel methodology for late-stage fluorination with fast reaction times and a broad substrate scope (scheme 1). This approach achieves high yields even for complex substrates like amino acids and nucleotides, despite only requiring substoichiometric quantities of bromine and silver nitrate as co-reactants.



- ✓ Mild conditions
- ✓ Fast reaction times
- ✓ Broad functional group compatibility (38 substrates)

Scheme 1. Bromine and silver nitrate mediated desulfurative fluorination

References

[1] Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37* (2), 320–330.
[2] Canestrari, D.; Lancianesi, S.; Badiola, E.; Strinna, C.; Ibrahim, H.; Adamo, M. F. A. *Org. Lett.* **2017**, *19* (4), 918–921.
[3] Canestrari, D.; Cioffi, C.; Biancofiore, I.; Lancianesi, S.; Ghisu, L.; Ruether, M.; O'Brien, J.; Adamo, M. F. A.; Ibrahim, H. *Chem. Sci.* **2019**, *10* (39), 9042–9050.
[4] York, C.; Surya Prakash, G. K.; Olah, G. A. *Tetrahedron* **1996**, *52* (1), 9–14.

Visible-Light-Mediated Trifluoromethylation/Ring Closure Sequences of 2-Vinyl Phenols: Synthesis of Trifluoromethylated 4*H*-Chromene Derivatives

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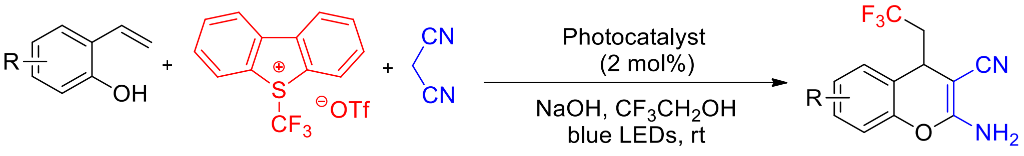
The introduction of a trifluoromethyl moiety into biologically active compounds usually leads to improvement of their physical properties and biological activities [1]. The radical trifluoromethylation to alkenes is among the most direct approaches for the construction of C–CF_3 bonds, which uses electrophilic and nucleophilic trifluoromethylation reagents in the presence of various types of reductants or oxidants. *ortho*-Quinone methides are versatile synthons that are frequently used as 1,4-dipoles and Michael acceptors. As part of the research program related to redox reactions and cyclization sequences, we recently reported intramolecular redox reactions [2] and radical addition and ring expansion reactions of alkenes with several radical sources under redox conditions[3]. In this presentation, visible light-mediated photocatalytic trifluoromethylation, single electron transfer (SET) oxidation, and cycloaddition cascades of 2-vinyl phenols with Umemoto's reagent and malononitrile were developed. This approach provided the multicomponent synthesis of trifluoromethylated 4*H*-chromenes via the *in situ* generation of *o*-quinone methides, followed by sequential cyclization [4].



References

[1] (a) Xu, X. H. ; Matsuzaki, K. ; Shibata, N. *Chem. Rev.*, **2015**, *115*, 731-764. (b) Zhu,Y.; Han, J. Wang, J.; Shibata, N.; Sodeoka, M.; Soloshonok, V. A.; Coelho, J. A. S.; Toste, F. D. *Chem. Rev.*, **2018**, *118*, 3887-3964. [2] For a selection of our recent studies on C–H activation, see: (a) Kang, Y. K.; Kim, S. M.; Kim, D. Y. *J. Am. Chem. Soc.*, **2010**, *132*, 11847-11848; (b) S. J. Kwon, D. Y. Kim, *Chem. Rec.*, **2016**, *16*, 1191-1203. (c) C. W. Suh, S. J. Kwon, D. Y. Kim, *Org. Lett.*, **2017**, *19*, 1334-1337. [3] (a) Kwon, S. J.; Kim, D. Y. *Org. Lett.*, **2016**, *18*, 4562-4565. (b) Jung, H. I.; Kim, Y.; Kim. D. Y. *Org. Biomol. Chem.*, **2019**, *17*, 3319-3323. (d) Kim, Y. J.; Kim, D. Y. *Org. Lett.*, **2019**, *21*, 1021-1025. [4] (a) Jang, J.; Kim. D. Y. *Asian J. Org. Chem.*, **2021**, *10*, 3271-3274. (b) Jang, J.; Kim. D. Y. *Asian J. Org. Chem.*, **2022**, e2202200531.

The Synthesis of *N*-substituted Hydroxamic Acids via a Pentafluoropyridine Mediated Procedure

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The ability to make esters, amides and other carbonyl-based functionality through activated carboxylic acid intermediates is highly prized. Previously, we have developed methodology for accessing similar functional groups via acyl fluorides through a deoxyfluorination process mediated by pentafluoropyridine (PFP).[1] Our work has since focused on using this as a new coupling agent for *N*-substituted hydroxamic acid formation. This unusual amide-like functional group is present in several natural products including hydroxamate siderophores. These microbial iron chelators contain hydroxamic acid functionality distributed throughout, providing multiple key bidentate binding sites. Their high affinity towards Fe ions plays a key role in the regulation of iron through uptake, transport and storage.[2] We believe that the PFP methodology provides an improvement to previous *N*-substituted hydroxamic acid formation strategies also allowing for the use of ^{19}F NMR tracking to quantify conversion to the activated intermediate. Hence, this has been applied to a range of carboxylic acids including alkyl, electron-poor & electron rich aromatic, heteroaromatic as well as the coupling to medicinally relevant acids.

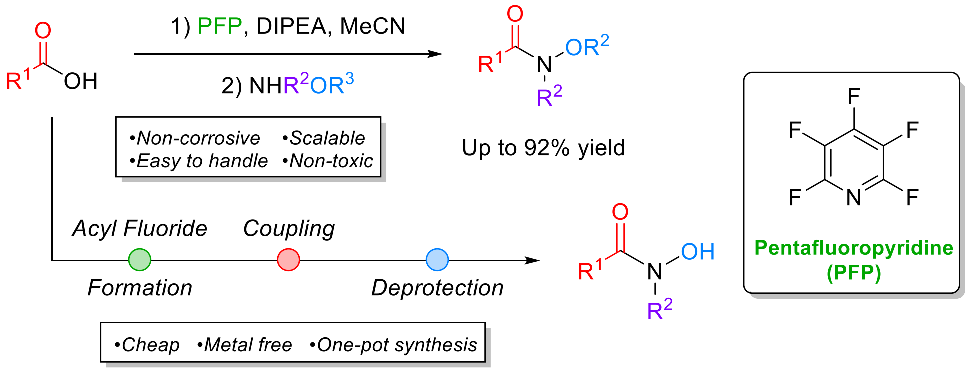

Figure 1. The synthesis of *N*-substituted hydroxamic acids as an isolatable protected intermediate or directly in a one-pot procedure, mediated by pentafluoropyridine.

References:
[1] (a) *Org. Lett.*, **2021**, 23(15), 5793–5798 (b) *Org. Biomol. Chem.*, **2022**, 20(41), 8059-8064.
[2] (a) *Annu. Rev. Phytopathol.*, **2008**, 46, 149–187 (b) *Nat. Prod. Rep.*, **2014**, 31(10), 1266-1276 (c) *J. Chem. Soc., Dalton Trans.*, **1992**, 22 3265–3271.

Mild C–F Activation of Perfluoroalkyl Substances by α-Fluorine Substitution of Perfluoroalkyl Azides With Thiols

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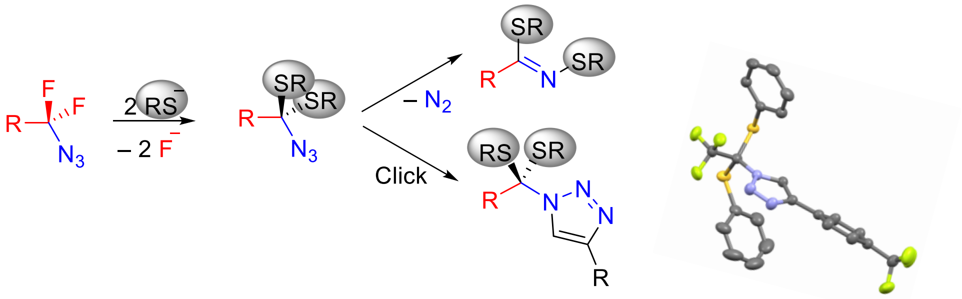
Perfluoroalkyl substances (PFAS) are synthetic chemicals with strong C–F bonds, making them highly resistant to chemical and thermal degradation.[1] Widespread use of PFAS in industrial and consumer applications has led to their global distribution in water, soil, air, and biological systems, posing significant health and environmental risks. Current PFAS remediation strategies, such as adsorption, incineration, and electrochemical methods, face challenges in scalability, efficiency, and by-product toxicity.[2]

This study introduces a novel, mild, and selective chemical process for activating and functionalizing C–F bonds in PFAS through α-fluorine substitution in fluorinated azides.

Perfluoroalkyl azides, emerging as stable and versatile intermediates,[3] were hypothesized to undergo nucleophilic attack at the terminal nitrogen of the azide group. This process enables fluoride elimination and the creation of an electrophilic reactive site for further nucleophilic addition–elimination reactions. Using weakly basic thiolates, fluorine substitution proceeds under mild conditions to yield disubstituted products with unprecedented reactivity (Scheme 1).



Scheme 1. Mild and scalable C(sp^3)–F substitution of azides. Denitrogenation/rearrangement of primary products- reactivity and application.

Acknowledgements

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References

[1] Perfluoroalkyl Substances (Ed. Ameduri, B.), RSC, London, **2022**.
[2] Longendyke, G. K.; Katel, S.; Wang, Y. *Environ. Sci.: Processes Impacts*, **2022**, *24*, 196–208.
[3] Bakhanovich, O.; Beier, P. *Chem. Eur. J.* **2020**, *26*, 773–782.

Use of Cyclic Sulfoximines as (Deutero)(fluoro)methylation Reagents

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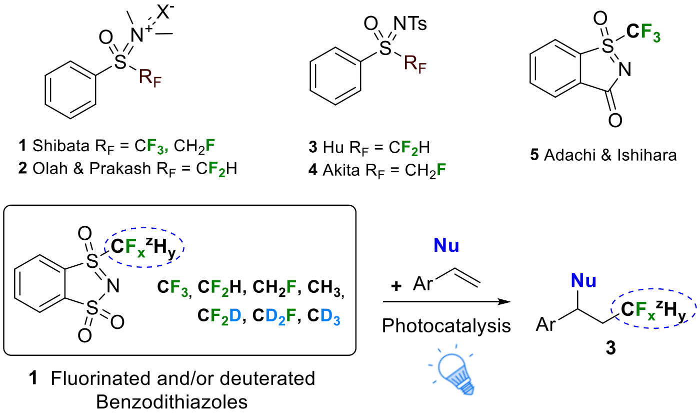
Fluoroalkylated sulfoximines are significantly involved in the numerous advances in fluoromethylation made recently, as electrophiles and radical donors. We can cite the work of Shibata **1** [1], Hu **3** [2] and Akita **4** [3] in this field. Our group has contributed to these advances, [6] focusing in particular on cyclized fluorinated sulfoximines inspired by the work of Adachi and Ishihara. [7] An efficient synthetic route to these sulfoximines **1**, analogues of benzodithiazoles with $-CF_xH_y$ groups, has been developed. [8]

We will present optimized scale-up syntheses of these benzodithiazoles, essential for their use as reagents. Their radical reactivities in photoredox catalysis **3** will be studied, highlighting the advantages of this new structure over more conventional sulfoximines. Moreover, easy deuteration of these benzodithiazoles allows them not only to react as $\bullet CF_xH_y$ donors (from $\bullet CF_3$ to $\bullet CH_3$), but also as $\bullet CF_xD_y$ donors, forming unique functional groups.



Scheme 1. Use of Cyclic Sulfoximines as (Deutero)(fluoro)methylation Reagents.

References

[1] Noritake, S.; Shibata, N.; Nakamura, S.; Toru, T.; Shiro, M. *Eur. J. Org. Chem*. **2008**, 3465-3468.
[2] Zhang, W.; Wang, F.; Hu, J. et al. *Org. Lett*. **2009**, 11, (10), 2109-2112.
[3] Noto, N.; Koike, T.; Akita, M. et al. *ACS Catal*. **2019**, 9, (5), 4382-4387.
[4] Liang, J.; Wang, G.; Dong, L.; Pang, X.; Qin, J.; Xu, X.; Shao, X.; Li, Z. *Org. Lett.* **2021**, 23, (14), 5545-5548.
[5] Pégot, B.; Urban, C.; Bourne, A.; Le, T. N.; Bouet, S.; Marrot, J.; Diter, P.; Magnier, E. *Eur. J. Org. Chem*. **2015**, 3069.
[6] Adachi, K., Ishihara, S. *Japan Tokkyo Kokai Patent*, **2005,** 145917.
[7] Duhail, T.; Messaoudi, S.; Dagousset, G.; Marrot, J.; André-Barrès, C.; Magnier, E.; Anselmi, E. *Adv. Synth.Catal.* **2023**, 365, 2392-2399.

Diaminomethylation of Fluoropyridines

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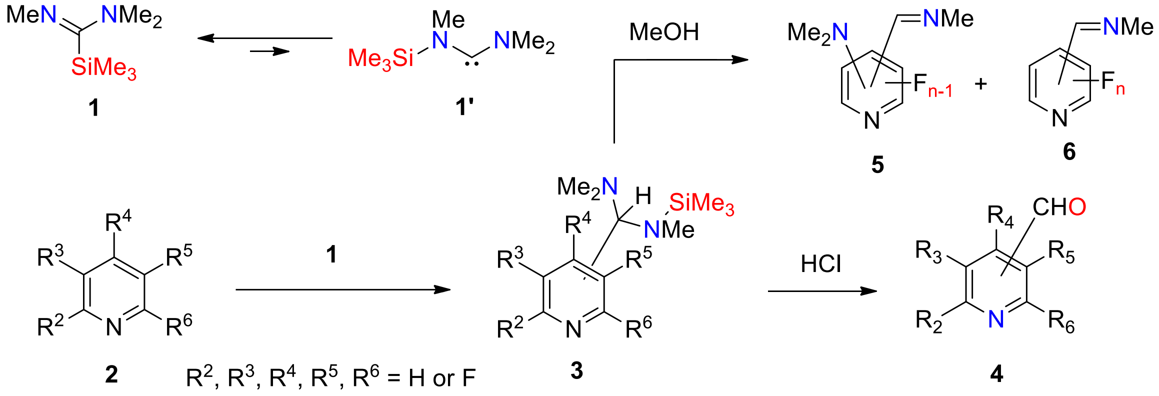
C-silylformamidine **1** was found to exist in equilibrium with its carbene tautomer **1'**. Formylation of fluoropyridines **2** using silylformamidine **1** was successfully carried out via a two-step, catalyst-free procedure. A variety of fluoropyridines containing one to four fluorine atoms were subjected to this reaction. In certain cases, the reaction proceeded through C–H insertion at the β- or γ-position of the pyridine ring, leading to the formation of aminal intermediates **3**. Subsequent hydrolysis of aminals **3** predominantly yielded the corresponding aldehydes **4**. Density Functional Theory (DFT) calculations suggest that the reaction mechanism involves deprotonation of the pyridine by carbene **1'**, acting as a strong base, followed by rearrangement of the resulting tight ion pair into the final product. An alternative pathway—nucleophilic addition of **1'** to the pyridine carbon followed by hydrogen transfer via a strained three-membered transition state—was calculated to require significantly higher activation energy.



Scheme 1. Rection of fluoropyridines with silylformamidine **1**.

Aminals **3** were also subjected to methanolysis at room temperature, which produced a mixture of compounds **5** and **6**. During this transformation, the aminal group was converted into a methylimine, and in some cases, a dimethylamino group substituted a fluorine atom. The relative proportions of pyridine methylimine products bearing a dimethylamino group versus those without it were determined for each fluoropyridine derivative. These products were also further hydrolyzed to afford the corresponding aldehydes.

References

[1] G. Koidan, S. Zahorulko, A. Hurieva, T. Shvydenko, E.B. Rusanov, A.B. Rozhenko, U. Manthe, A. Kostyuk, *Chemistry – A European Journal* **2023**, e202301675.

[2] G. Koidan, S. Zahorulko, S. Filimonchuk, S. Shishkina, E.B. Rusanov, A. Kostyuk, Methanolysis of Fluoropyridine Aminals, *ChemistrySelect* **2025**, *10*, e202500101.

Organometallic Chemistry

Benzimidazole-2-ylidene-Silver(I) Complexes Bearing the 4-trifluoromethoxy Group As Organofluorine Compounds: Synthesis, Characterization, and Inhibitory Properties Against Some Metabolic Enzymes

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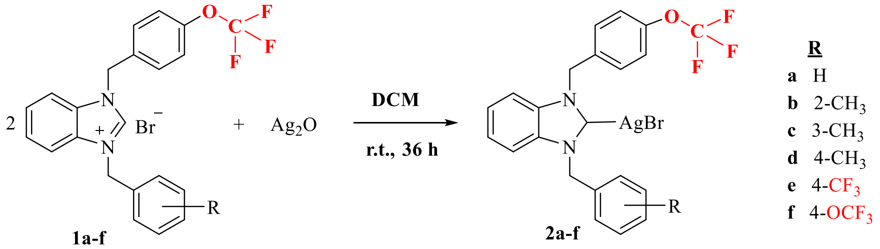
Organofluorine compounds have attracted significant attention in various fields due to their physicochemical, electrochemical and biological properties. Fluorine has high electronegativity. Thus, the presence of fluorine in organofluorine compounds provides low polarizability, high dipole moments, small volume and formation of strong C–F bonds. The addition of fluorine to drug active ingredients affects various pharmacological properties of drug candidates such as metabolic stability, membrane permeability, lipophilicity and binding affinity [1].



Scheme 1. Synthesis of NHC-Ag(I) complexes bearing trifluoromethoxy group.

Metal-based drugs are effective in the treatment of various diseases especially cancer. Although metal-containing drugs such as cisplatin, fluorouracil are known as effective therapeutics, N-Heterocyclic carbene (NHC) silver complex is one of the metalloorganic compounds that have attracted interest in recent years [2]. This study includes the synthesis and enzyme inhibition (CAs and AChE) activity of NHC-Ag(I) complexes containing fluorinated groups. The structures of all synthesized complexes were elucidated by appropriate spectroscopic methods (^{1}H NMR, ^{13}C NMR, ^{19}F NMR and FT-IR).

Acknowledgment
This study was financially supported by Inonu University Research Fund (Project Code: FBA-2024-3684).

References

[1] Harsanyi, A., Sandford, G., Green Chem., **2015**, 17, 2081–2086.

[2] A. Behçet, A., Aktaş, A., Gök, Y., Kaya, R., Taslimi, P., Gülçin, İ., *Journal of Heterocyclic Chemistry*, **2021**, *58*(*2*), 603.

Synthesis and Characterization of Pd(II) Metal Complexes Derived from N-Heterocyclic Carbenes with Fluorinated Substituents

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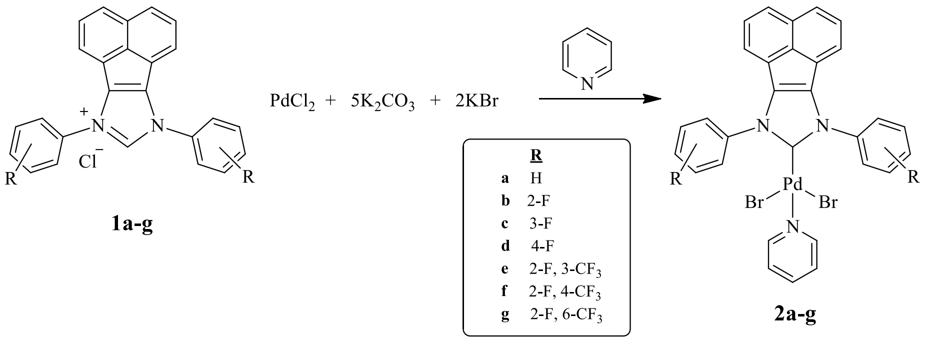
In recent years, the importance of green chemistry has significantly increased. The utilization of supercritical carbon dioxide ($scCO_2$) solvent systems provides a secure solvent environment, effectively aligning with numerous principles of green chemistry. The primary drawback of operating in a $scCO_2$ solvent environment is the insolubility of the organometallic compounds employed in this media. The incorporation of fluorine groups in the chosen materials enhances their solubility in the $scCO_2$ solvent medium [1].



Scheme 1. Synthesis of acenaphthyl-backboned NHC-Pd(II)-Pyridine complexes with fluorinated substituents

This study involved the synthesis of novel Pd(II) metal complexes obtained from N-heterocyclic carbenes (NHCs) including fluorinated substituents in the N-aryl region and an acenaphthyl framework. The characterization of all synthesized structures was conducted by spectroscopic techniques, including ^{1}H, ^{13}C, ^{19}F NMR, FTIR, elemental analysis, and HR-MS. These organometallic compounds will serve as catalysts in the supercritical carbon dioxide solvent environment.

Acknowledgment

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References

[1] Crone, M.; Türk, M. *Fluids*, **2023**, *8*(4), 121.

From Trifluoromethyl to Pentafluoroethyl: New Approaches in Gold(III) Complexes Stabilization

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In the last two decades the organometallic chemistry of gold has undergone significant developments, both in oxidation states I and III. Despite that, stabilization of Au(III) species is not always straightforward. A synthetic strategy for achieving this is based on the use of polydentate ligands such as P^C, N^C, C^N^C, or N^C^C.[1] Alternatively, the use of trifluoromethyl as a ligand has proven to be an effective tool for the development of this chemistry. In general, the marked group electronegativity of CF_3 and its relatively small size facilitate the stabilization of *late* transition metal complexes in high oxidation states.[2] Although diverse Au(III) trifluoromethyl complexes have been reported, their analogues containing longer perfluoroalkyl chains remain scarce.[3]

Recently, in our research group, a wide range of Au(III) complexes stabilized by trifluoromethyl ligands have been prepared, with general formulae $[PPh_4][Au^{III}(CF_3)_2(X)_2]$, $[PPh_4][Au^{III}(CF_3)_3(X)]$ (X = F, Cl, Br, I, CN), and $[Au^{III}(CF_3)_3L]$ (L = NCMe, OEt_2, CN^tBu, py, PR_3, tht).[4] Now, we have focused our attention on longer perfluoroalkyl ligands, in particular the pentafluoroethyl. In this communication we report the synthesis and characterization of novel Au(III) complexes stabilized by C_2F_5 ligands.

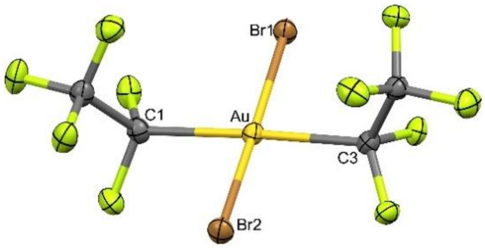

Figure 1. X-Ray structure of the $[PPh_4][Au(C_2F_5)_2Br_2]$ complex.

References

[1] a) Herrera, R. P.; Gimeno, M. C. *Chem. Rev.* **2021**, *121*, 8311-8363. b) Rocchigiani, L.; Bochmann, M. *Chem. Rev,* **2021**, *121*, 8364-8451.

[2] García-Monforte, M. A.; Martínez-Salvador, S.; Menjón, B. *Eur. J. Inorg. Chem*. **2012**, 4945-4966.

[3] a) Portugués, A.; López-García, I.; Jiménez-Bernad, J.; Bautista, D.; Gil-Rubio, J. *Chem. Eur. J.* **2019**, *25*, 15535-15547. b) Rachor, S. G.; Müller, R.; Wittwer, P.; Kaupp, M.; Braun, T. *Inorg. Chem*. **2022**, *61*, 357-367.

[4] a) Martínez-Salvador, S.; Falvello, L. R.; Martín, A.; Menjón, B. *Chem. Eur. J.* **2013**, *19*, 14540-14552. b) Pérez-Bitrián, A.; Baya, M.; Casas, J. M.; Martín, A.; Menjón, B.; Orduna, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 6517-6521. c) Pérez-Bitrián, A.; Martínez-Salvador, S.; Baya, M.; Casas, J. M.; Martín, A.; Menjón, B.; Orduna, J. *Chem. Eur. J.* **2017**, *23*, 6919-6929. d) Pérez-Bitrián, A.; Baya, M.; Casas, J. M.; Falvello, L. R.; Martín, A.; Menjón, B. *Chem. Eur. J.* **2017**, *23*, 14918-14930.

Activation of Perfluoro(methyl vinyl ether) at Rh(I) Phosphine Complexes: Metal-Centered versus Phosphine Mediated Decarbonylation

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This study investigates the reactivity of perfluoro(methyl vinyl ether) [PMVE, $CF_2{=}CF(OCF_3)$] towards rhodium(I) phosphine complexes, focusing on the C-F and C-O bond activation mechanisms and decarbonylation processes. Using the complex $[Rh(H)(PEt_3)_3]$, we observed unprecedented reactivity pathways that are distinguish from previously studied fluoroolefins.[1-4] Notably, in addition the coordination of PMVE to the Rh-centre at $[Rh(H)(PEt_3)_3]$ and insertion of it into the Rh-H bond, the intermediate $[Rh(CF_2CFHOCF_3)(PEt_3)_3]$ undergoes β-OCF_3 elimination. Furthermore, PMVE can insert into the Rh-F bond in *trans*-$[Rh(F)(CO)(PEt_3)_2]$ leading to the formation of the *trans*-$[Rh(CO)(CF(OCF_3)CF_3)(PEt_3)_2]$. These reaction pathways offer a new route for metal-centered mediated decarbonylation at room temperature and open a new door for possible installation of the -$CF(OCF_3)CF_3$ group into organic molecules. Remarkably, this study highlights PMVE as an effective CO source, which is released not only through interaction with rhodium but also via a metal-free, phosphine-mediated process promoting the decarbonylation reaction. The latter is assessed by oxidative addition of PMVE at triethylphosphine to form fluorophosphoranes, $(OCF_3)CF{=}CF(PFEt_3)$, which subsequently release carbon monoxide gas upon decomposition.

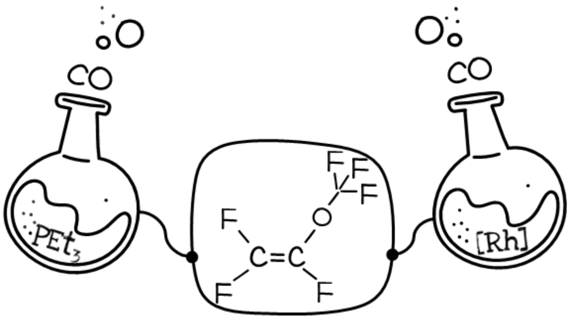

Figure 1. Schematic illustrating the CO production upon the reactivity of PMVE towards rhodium complexes and phosphine.

References

[1] Talavera, M.; Mollasalehi, S.; Braun, T. *Chem. Sci.* **2024**, *15*, 8472-8477.
[2] Talavera, M.; Braun, T. *Chem. Sci.* **2022**, *13*, 1130-1135.
[3] Talavera, M.; Braun, T. *Chem. Eur. J.* **2021**, *27*, 11926-11934.
[4] Talavera, M.; Braun, T. *Synlett* **2020**, *31*, 1760-1774.

Semi-catalytic Trifluoromethylation Using Tetrakis(trifluoromethylcopper)

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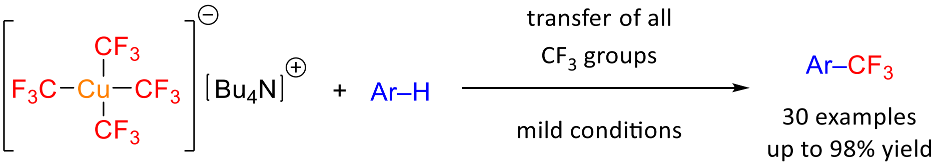
The trifluoromethyl group plays a crucial role in the pharmaceutical and agrochemical industries. The incorporation of the trifluoromethyl group into drug candidates can boost their chemical and metabolic stability and enhance properties, such as lipophilicity, bioavailability, and protein binding affinity.[1] Direct trifluoromethylation — especially when mediated or catalyzed by transition metals — represents one of the most promising and efficient approaches. Generally, the trifluoromethyl group can be introduced into organic molecules via nucleophilic, electrophilic, or free radical mechanisms.[2]

Organocopper(III) species are widely regarded as essential intermediates in various cross-coupling reactions, aerobic oxidations, and enzyme-catalyzed processes. However, these complexes are typically thermally unstable and difficult to isolate, which presents significant challenges for both their study and practical implementation.[3]

The trifluoromethyl group stands out as a unique class of ligands capable of stabilizing high-valent organocopper(III) species. Trifluoromethyl copper(III) complexes have proven effective for C–H trifluoromethylation of arenes, alkenes, alkynes, and C(sp^3)–H bonds.[3–5] One of the most extensively studied compounds in this class is $[Cu(CF_3)_4][Bu_4N]$, which is generally considered inert as a trifluoromethylation agent.[6] Here we present the first application of $[Cu(CF_3)_4][Bu_4N]$ for trifluoromethylation reactions, capable of transferring up to four trifluoromethyl groups.



Scheme 1. The application of $[Cu(CF_3)_4][Bu_4N]$ for trifluoromethylation reactions.

References

[1] Kirsch, P. Modern Fluoroorganic Chemistry, WILEY-VCH, **2004**.
[2] Chu, L.; Qing, F. L. *Acc. Chem. Res*. **2014**, *47*, 1513–1522.
[3] Liu, H.; Shen, Q. *Coord. Chem. Rev*. **2021**, *442*, 213923.
[4] Motornov, V.; Klepetářová, B.; Beier, P. *Adv. Synth. Catal*. **2023**, *365*, 2858–2864.
[5] Motornov, V.; Procházka, M.; Alpuente, N.; Salvador, P.; Slavíček, P.; Klepetářová, B.; Ribas, X.; Beier, P. *ChemistryEurope* **2024**, *2*, e202400004.
[6] Alayoglu, P.; Chang, T.; Yan, C.; Chen, Y. S.; Mankad, N. P. *Angew. Chem., Int. Ed.* **2023**, *62*, e202313744.

Pentafluoroethyl Stabilized α-Silyl Carbanions

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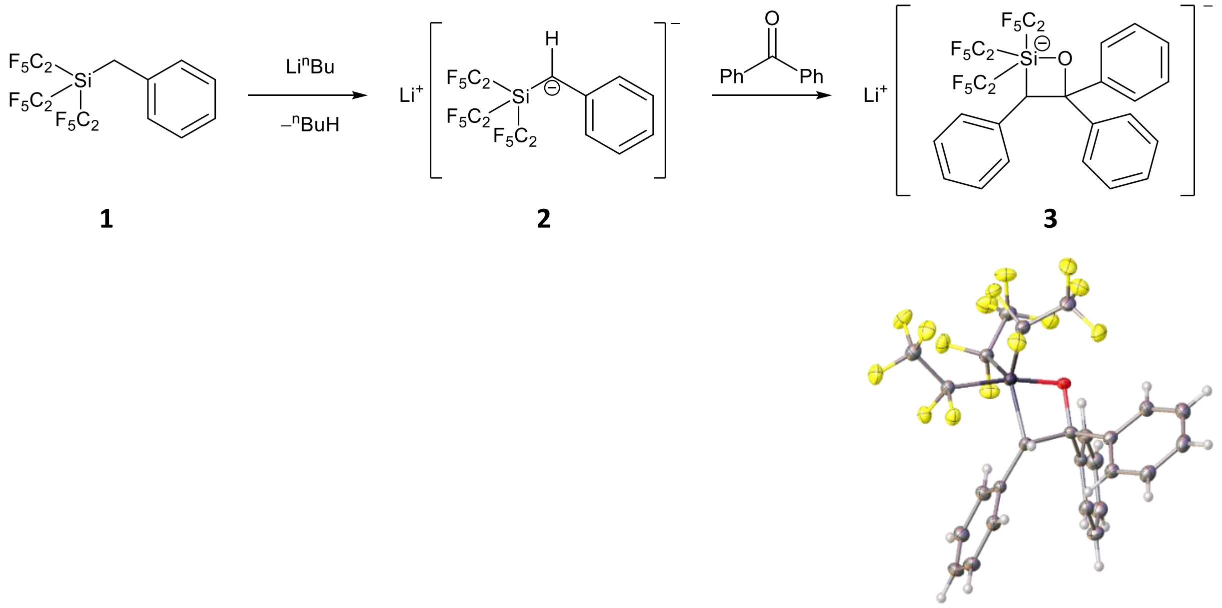
Since Peterson's publication of a new olefination method employing silyl-carbanions [1], there have been a number of different models for the reaction mechanism [2]. Although the reaction can be seen as the silicon equivalent of the Wittig reaction, evidence for a 4-membered cyclic intermediate is rare and the majority of experimental evidence seems to suggest a multi-step mechanism without a 4-membered ring intermediate [2]. Nevertheless, Okazaki *et al*. managed to isolate and structurally characterise one cyclic Peterson intermediate utilizing the electron withdrawing Martin ligand and hexafluoroacetone as a substrate [3].

In this poster we present the synthesis of silanes with electron withdrawing groups for the generation of stabilised α-silyl carbanions and from these the synthesis of several stable cyclic Peterson reaction intermediates.



Scheme 1. Generation of α-silyl carbanion **2** and subsequent reaction with benzophenone to form the stable cyclic Peterson intermediate **3**.

References

[1] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.
[2] van Staden, L. F.; Gravestock, D.; Ager, D. J. *Chem. Soc. Rev.* **2002**, *31*, 195.
[3] Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 7598.

Inorganic Chemistry

Novel Readily Available Lanthanide-Halide Complexes as Potential Precursors to Single Molecule Magnets

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Single Molecule Magnets (SMMs) are individual molecules that can function as nanoscale magnetic particles. These molecular nanomagnets exhibit strong magnetic anisotropy and can retain their magnetization for a relatively long time in the absence of an external field. [1] Since this phenomenon is purely molecular in origin it is fundamentally different from that of conventional bulk magnets such as AlNiCo and SmCo. This class of materials has attracted significant attention from the scientific community due to their potential applications in information storage, making them a significant topic in fields such as engineering and quantum computing. However, their widespread use is limited by a major drawback: SMM behaviour is typically observed only at very low temperatures. Currently, the best SMMs are lanthanide-based compounds. [2]

The performance of Ln-based SMMs is strongly dependent on the geometry of the lanthanide ion's coordination sphere, with species exhibiting axial symmetry being the most promising candidates for effective SMMs. Even small deviations from linearity enhance the magnetic relaxation of the SMM. To achieve optimal control over the geometry of the coordination sphere, Weakly Coordinating Anions (WCAs) can be employed as counterions, as they exert minimal distortion on the geometry of the complex cation. [3]

In our stude, we present a facile synthesis of novel lanthanide complexes of the types $[LnX_2]^+$ and $[LnX]^{2+}$ (Ln = Dy, Y, Er) as salts of perfluorinated and readily available WCA: $[Al(OC(CF_3)_3)_4]^-$. The structures of these complexes were determined using X-ray diffraction (XRD) showing linear X-Ln-X arrangement and strong dependence of coordination sphere on the type of auxiliary ligands used to stabilize the cationic species. Additional physicochemical studies, including vibrational spectroscopy (IR and Raman) and thermal stability analysis via TGA/DSC, were performed. The obtained data provide new insights into the properties of the synthesized salts, which may be valuable for further research on SMMs as precursors to more elaborate complexes.

References

[1] Marin, R.; Brunet, G.; Murugesu, M. *Angew. Chem. Int. Ed.,* **2021***, 60 (4),* 1728-1746.

[2] Guo, F.S.; Day, B. M.; Chen, Y.C.; Tong, M. L.; Mansikkamäki, A.; Layfield, R.A. *Science*, **2018**, *362*, 1400–1403.

[3] Riddlestone I. M.; Kraft A.; Schaefer J.; Krossing I. *Angew. Chem. Int. Ed.,* **2018**, *57*, 13982-14024.

Hydrodefluorination with Heterogenous Ziegler-Natta Catalysts

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Hydrodefluorination (HDF) exploiting immobilized Ti(III)-H species on heterogenous Ziegler-Natta (ZN) catalysts is demonstrated. Economical early transition metal catalyzed HDF has been described by Lentz *et al.* using Cp_2TiF_2 as the catalyst precursor (Cp = cyclopentadienyl);[1] a Ti(III) hydride, Cp_2TiH, was identified as the active species.[2] An inexpensive hydride source like diphenylsilane was used to regenerate the catalyst after HDF. Donor solvents, necessary to increase activity, are detrimental to selectivity. This drawback could be avoided by immobilization on a surface. Ziegler-Natta (ZN) catalysts are competent olefin polymerization catalysts that dominate the industrial production of isotactic polypropylene.[3–6] It has been shown that addition of H_2 can increase activity via regeneration of dormant sites and modulate molecular weight via hydrogenolysis of growing polymer chains.[7] This infers that Ti(III)-H species that have enough stability to survive for at least some time are produced intermittently.

Studies on model substrates such as fluorocyclohexane, perfluoropyridine, perfluorotoluene and perfluoroallylbenzene highlight the ability of ZN systems to engage in HDF. Activity and selectivity can be influenced by choice of ZN catalyst and hydrogen source used to regenerate the active species; on this regard, H_2 can be used as a cheaper and cleaner alternative to the more common silanes. Addition of an organic Lewis base[6] to the catalytic formulation affects both activity and selectivity towards HDF, showcasing the tunability of the system. Turnover numbers in the order of $>10^4$ can be inferred under the assumption that only 1% of the Ti particles on the catalyst are active (as in ZN olefin polymerization).[8] Multiple consecutive HDF steps are achieved and a variety of products are observed. HDF patterns highlight mixed reactivity between that of Lentz's original system and Lewis acidic catalysts, suggesting the presence of different active sites working simultaneously.

Traditional HDF catalysts employ rather expensive metals and display low activities.[9] ZN systems are cheap, tunable and a wealth of information from 70 years of research can be exploited. Selective HDF of per- and polyfluorinated substrates could yield novel building blocks for the pharmaceutical industry.

References

(1) Kühnel, M. F.; Lentz, D. *Angew. Chem. - Int. Ed.* **2010**, *49* (16), 2933–2936.
(2) Ehm, C.; Krüger, J.; Lentz, D. *Chem. – Eur. J.* **2016**, *22* (27), 9305–9310.
(3) Ziegler, K.; Holzkamp E.; Breil H.; Martin H. *Angew. Chem.* **1955**, *67*, 426.
(4) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710.
(5) Busico, V. *in* Kaminsky, W., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2013**.
(6) Addeo, A.; Pasquini, N. *Polypropylene Handbook*; **2006**.
(7) Vittoria, A.; Meppelder, A.; Friederichs, N.; Busico, V.; Cipullo, R. *ACS Catal.* **2020**, *10* (1), 644–651.
(8) Vittoria, A.; Meppelder, A.; Friederichs, N.; Busico, V.; Cipullo, R. *ACS Catal.* **2017**, *7* (7), 4509–4518.
(9) Whittlesey, M. K.; Peris, E. *ACS Catal.* **2014**, *4* (9), 3152–3159.

Synthesis of Fluorinated Zn(II) Coordination 2D Sheets with Adaptive Pore Structures for π-Hole-Induced Guest Encapsulation

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In the realm of chemical engineering and molecular science, the separation of molecules with similar shapes and sizes presents a significant challenge, particularly when employing conventional methods such as molecular sieving and adsorption. In this study, a novel fluorinated Zn(II) coordination 2D sheet, $[Zn(L)(py)]_{2n}$ (**1**), was synthesized using dinuclear Zn(II) centers, tetrafluoroisophthalic acid (H_2L), and pyridine (py). This material exhibits selective adsorption of small molecules, driven by quadrupole moments[1,2] induced in the framework via fluorination. The framework features uniaxial voids, constituting 12.6% of its total volume, which enhance selective molecular interactions. Adsorption isotherms for N_2, CO_2, and benzene exhibit type-I behavior, indicating effective host characteristics at low relative pressures. The framework demonstrates a notable CO_2 adsorption capacity, reaching 128% of the pore volume, demonstrating reversible and sufficient pore expansion upon guest uptake. Crystallographic analysis revealed that **1** undergoes a crystal-to-crystal transformation upon I_2 uptake, accompanied by interlayer expansion. Furthermore, replacing pyridine with picoline isomers yielded isostructural 2D sheets, $[Zn(L)(picoline)]_{2n}$ (2-picoline: **2**; 3-picoline: **3**; 4-picoline: **4**), where variations in pore shape lead to distinct molecular recognition behaviors. This study suggests that fluorination may influence molecular interactions and could be relevant to molecular separation technologies.

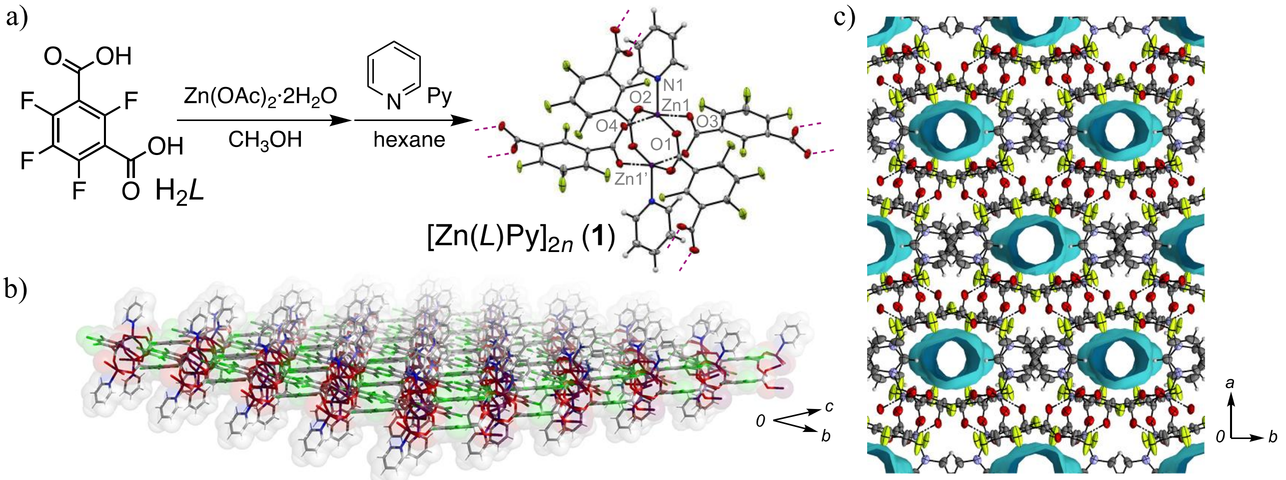

Figure 1. a) Preparation, b) a fragment of the 2D sheet, and c) the packing structure of **1**.

References

[1] K. Shimizu, M. F. C. Gomes, A. A. H. Padua, L. P. N. Rebelo, J. N. C. Lopes, *J. Phis. Chem. B*, **2009**, *113*, 9894-9900; [2] Y. Ikumura, T. Kawasaki, Y. Ishida, H. Usui, S. Uchida, K. Kamata, M. Nomura, A. Hori, *RSC Adv*., **2025**, *15*, 6184-6190.

Synthesis and Application of the Weakly Coordinating Anion $[CHB_{11}F_{11}]^-$

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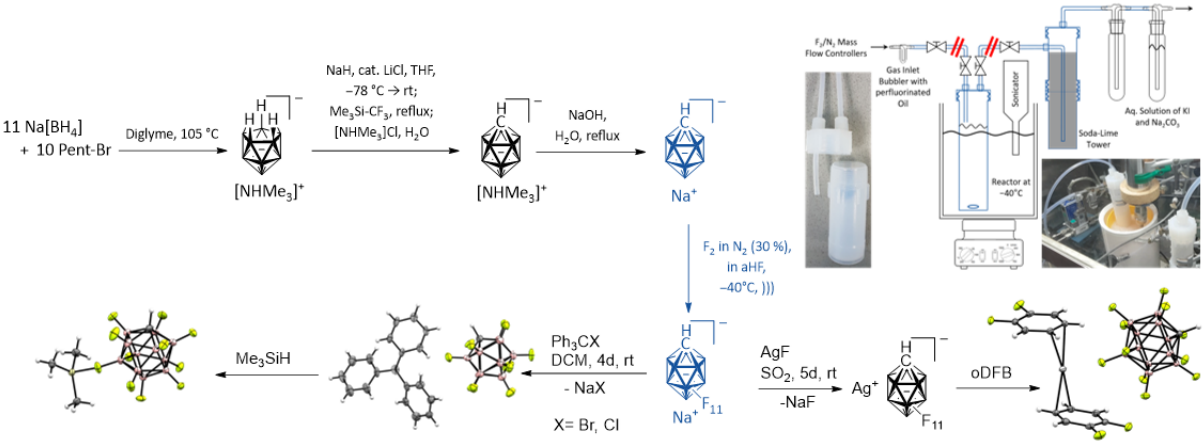
The undecafluorinated carbaborate $[CXB_{11}F_{11}]^-$ (X = H, alkyl) as a weakly coordinating anion (WCA) is known for its exceptional stability towards small, electrophilic, Lewis acid cations.[1] With a potential prohibition on PFAS being discussed, which covers a variety of established WCAs, $[CHB_{11}F_{11}]^-$ emerges a promising WCA for fundamental and commercial applications. The availability of the anion is determined by the synthesis, with fluorination being a key step and fundamental for the use of $[CHB_{11}F_{11}]^-$. We present the improved and upscaled synthesis protocols of $[CB_{11}H_{12}]^-$ [2] and $[CHB_{11}F_{11}]^-$, along with its application for the synthesis of reactive cations. In an open-flow system with 30% F_2 gas at −40°C and ultrasound, the fluorination of up to 10g of $[CHB_{11}F_{11}]^-$ is achieved, which is the largest synthesis in terms of amount to date.[3] Furthermore, salt metathesis reactions have been employed to synthesize useful precursors for the introduction of the anion, including the silver(I) and trityl cation, $[Ag(\textit{o}dfb)_2][CHB_{11}F_{11}]$ and $[Ph_3C][CHB_{11}F_{11}]$.[3] This enables the generation of strong Lewis acid cations, such as $[Me_3Si][CHB_{11}F_{11}]$[1c], opening up a broad field of further chemistry.



Scheme 1. Synthesis protocol of $Na[CHB_{11}F_{11}]$ and subsequent reactions to useful salts. Fluorination setup.

References

[1] a) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 13982 b) C. Douvris, J. Michl, *Chem. Rev.* **2013**, *113*, PR179-233. c) T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2007**, *46*, 6346. d) S. V. Ivanov, D. V. Peryshkov, S. M. Miller, O. P. Anderson, A. K. Rappé, S. H. Strauss, *J. Fluorine Chem.* **2012**, *143*, 99.

[2] a) L. Toom, A. Kütt, I. Leito, *Dalton Trans.* **2019**, *48*, 7499. b) J. Pecyna, I. Rončević, J. Michl, *Molecules (Basel, Switzerland)* **2019**, *24*. c) S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *J. Am. Chem. Soc.* **1998**, *120*, 4224.

[3] J. Kulenkampff, C. Armbruster, J. Drolshagen, C. Regnat, T. Wienold, L. Spari, J. Fix, T. Sterbak, H. Scherer, I. Krossing, *Chemistry - Methods* **2024**, e202400011.

From Stable Halogenated Superelectrophilic Tritylcations to Corresponding Luminescent Tritylradicals and their Peroxides

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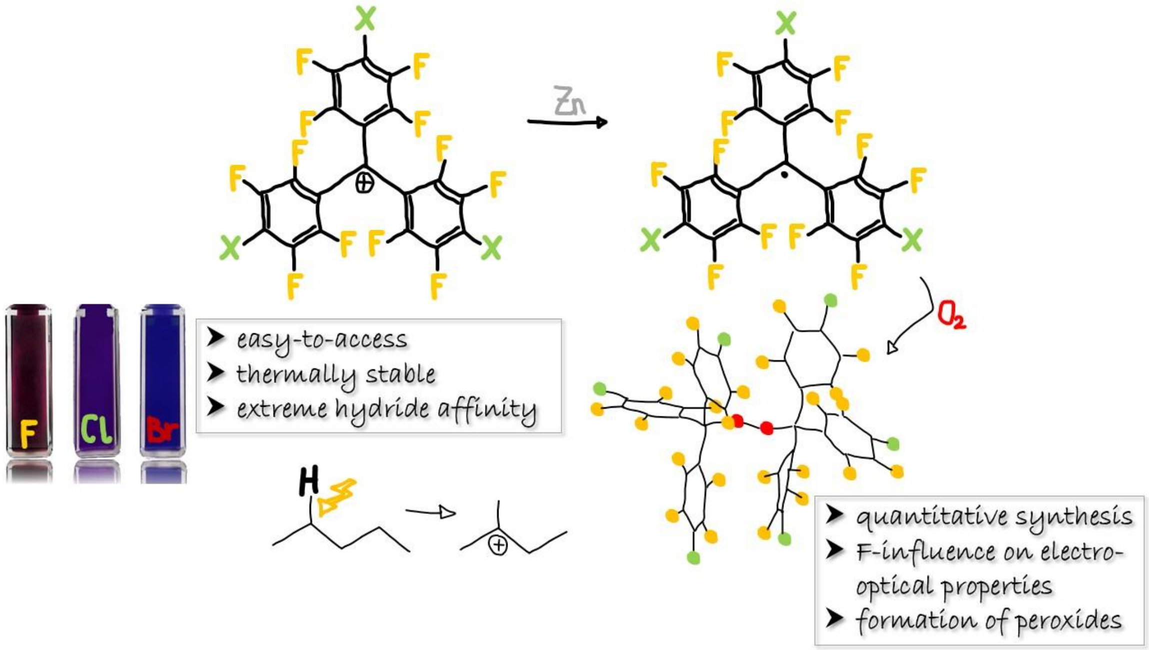
Herein we report on easy-to-access, superelectrophilic halogenated tritylcations, that are much more stable than their perfluorinated analogue and can be handled at room temperature for at least one day.[1] Their enormous electrophilicity enables them to abstract a hydride ion even from short-chain alkanes, like *n*-pentane and *n*-butane.

By adding an excess of zinc powder to a solution of these tritylcations, the respective radicals are obtained in quantitative amounts. In the last decades halogenated tritylradicals have attracted a lot of attention for their luminescent properties.[2] Due to their open-shell nature they could outperform classic organic closed-shell emitters. Fluorinated representatives, however, are still scarce as they suffer from synthetic challenges. Herein, we present three halofluoro tritylradicals prepared by a different synthetic approach starting from the corresponding cation. The influence of fluorine ligands on their electro-optical properties is investigated as well as their reactivity towards oxygen leading to the formation of respective peroxides.



References

[1] J. Schlögl, A. L. Brosius, A. N. Toraman, A. Wiesner, C. Müller, S. Steinhauer, S. Riedel, *Angew. Chem. Int. Ed.* **2025**, e202423857.

[2] A. Mizuno, R. Matsuoka, T. Mibu, T. Kusamoto, *Chem. Rev.* **2024**, *124*, 1034−1121.

$CF_3OCH_2C(O)OH$ and $(CF_3)_2NCH_2C(O)OH$ – Two Partially Fluorinated Acids

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Fluorine containing moieties are omnipresent in pharmaceuticals, in agrochemicals, and in a wealth of different materials that are relevant for diverse applications [1]. Hence, there is broad interest in developing versatile and easy-to-handle fluorinated building blocks that are accessible on large scale. Two examples for such building blocks are 2-trifluoromethoxyacetic acid $CF_3OCH_2C(O)OH$ and *N,N*-bis(trifluoromethyl)glycine $(CF_3)_2NCH_2C(O)OH$. The key step in their syntheses is the formation of salts of the anions $\{OCF_3\}^-$ and $\{N(CF_3)_2\}^-$ starting from $CF_3SO_2OCF_3$ and $CF_3SO_2N(CF_3)_2$ and a fluoride ion source, respectively [2,3]. An improved synthesis for the preparation of $CF_3SO_2OCF_3$ starting from triflic acid anhydride and triflic acid was developed [2] while the sulfonamide $CF_3SO_2N(CF_3)_2$ was obtained on large scale by electrochemical fluorination (ECF) of $CF_3SO_2N(CH_3)_2$ [4]. A straightforward two-step protocol starting from salts of $\{OCF_3\}^-$ and $\{N(CF_3)_2\}^-$ provided access to the respective acids $CF_3OCH_2C(O)OH$ and $(CF_3)_2NCH_2C(O)OH$ that both were characterized in detail. They are comparably strong acids with pK_a values of 2.7 and 2.9 respectively, showing the electron-withdrawing nature of the substituents $-OCF_3$ and $-N(CF_3)_2$ [2,5].

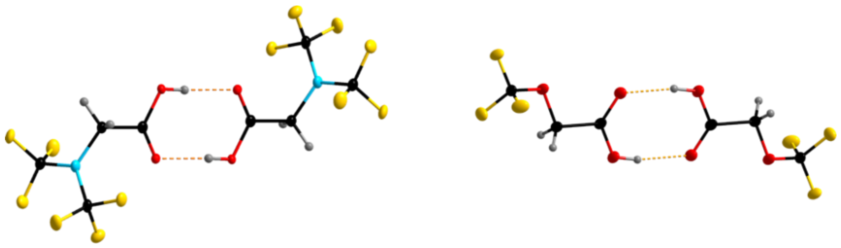

Figure 1. Dimers of $(CF_3)_2NCH_2C(O)OH$ and $CF_3OCH_2C(O)OH$ in the solid state.

References

[1] Kirsch, P. *Modern Fluoroorganic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2013**.
[2] Meier, T.; Lorenzen, S.; Knuplez, T.; Preitschopf, T.; Koppe, K.; Barthen, P.; Bertermann, R.; Schulte, M.; Ignat'ev, N. V.; Finze, M. *J. Fluorine Chem.* **2025**, *282*, 110396.
[3] Schneider, L. N.; Tanzer Krauel, E.-M.; Deutsch, C.; Urbahns, K.; Bischof, T.; Maibom, K. A. M.; Landmann, J.; Keppner, F.; Kerpen, C.; Hailmann, M.; Zapf, L.; Knuplez, T.; Bertermann, R.; Ignat'ev, N. V.; Finze, M. *Chem. Eur. J.* **2021**, *27*, 10973–10978.
[4] Sartori, P.; Ignat'ev, N.; Datsenko, S. *J. Fluorine Chem.* **1995**, *75*, 157–161.
[5] Breitenstein, C.; Ignat'ev, N.; Frank, W. *J. Fluorine Chem.* **2018**, *210*, 166–177.

Bis(perfluoroorganyl)diselanes and -ditellanes

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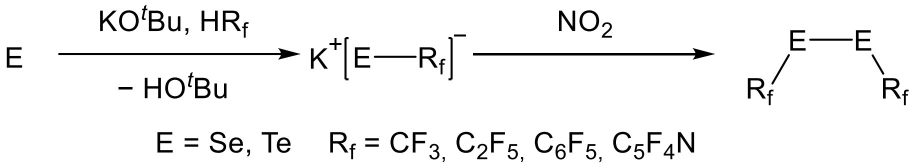
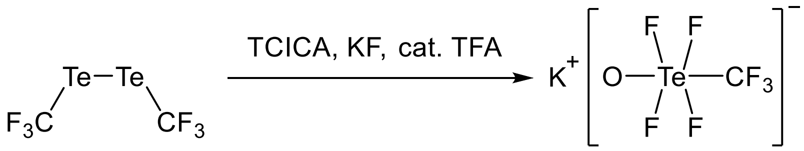
Diselanes and ditellanes are known to be valuable starting materials for the synthesis of selenium- and tellurium-containing compounds [1,2]. Bis(perfluoroorganyl)diselanes and -ditellanes could be prepared in a new one-pot method by generating first perfluoroorganylselanides and -tellanides from elemental selenium and tellurium through treatment with KO^{t}Bu and various fluorinated alkanes or arenes and subsequent oxidation with NO_2. This method avoids harsh conditions and toxic or difficult to prepare starting materials. In addition, $Te_2(CF_3)_2$ was further oxidised to *trans*-$[OTeF_4CF_3]^-$, a new trifluoromethyl derivative of pentafluoroorthotellurate (teflate, $OTeF_5$), using a method established by *Togni et al.*[3]



Scheme 1. Synthesis of bis(perfluoroorganyl)diselanes and ditellanes by treating elemental selenium or tellurium with KOtBu and fluorinated alkanes or arenes, followed by oxidation with NO2.



Scheme 2. Preparation of $K[OTeF_4CF_3]$ via the oxidation of bis(trifluoromethyl)ditellane using TCICA and KF in the presence of catalytic amounts of TFA.

References

[1] A. Ivanova, P. Arsenyan, *Coord. Chem. Rev.* **2018**, *370*, 55.

[2] V. A. Potapov, *Organic Diselenides, Ditellurides, Polyselenides and Pollytellurides. Synthesis and Reactions.* In *Patai's Chemistry of Functional Groups* (Ed.: Z. Rappoport), Wiley, **2013**.

[3] D. Bornemann, C. R. Pitts, C. J. Ziegler, E. Pietrasiak, N. Trapp, S. Kueng, N. Santschi, A. Togni, *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 12604.

Fluoride-Ion Donor Properties of $MoOF_4$ and WOF_4

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Molybdenum and tungsten oxide tetrafluoride ($MoOF_4$ and WOF_4) are moderate-strength Lewis acids and act as fluoride-ion acceptors. Salts of the MOF_5^- and $M_2O_2F_9^-$ {M = Mo or W} anions have been structurally characterized, and many neutral hexacoordinated $MOF_4(L)$ complexes are known with L = neutral organic ligand. We synthesized heptacoordinated $MOF_4(L–L)$ {L–L = bidentate ligand} complexes and were able to abstract a fluoride ion, yielding hexacoordinated ligand-stabilized $[MOF_3(L–L)]^+$ cations. Since the hepta- and octacoordinated cationic species $[WF_5(py)_n]^+$ and $[WF_5(L–L)]^+$ {n = 2,3: L–L = 2,2′-bipy or 1,10-phen} have been prepared,[1,2] heptacoordinated $[MOF_3(L–L–L)]^+$ {L–L–L = tridentate ligand} cations are targeted. To study these cationic species, tridentate ligands, such as terpyridine (terpy) and 1,4,7-trimethyl-1,4,7-triacyclononane (Me_3TACN), are used to access ligand-stabilized oxide fluoride cations with a coordination number of 7. Cation formation via ligand-induced autoionization and fluoride-ion abstraction will be discussed.

References

[1] Turnbull. D, Hazendonk. P, Wetmore. S. D, Gerken. M, *Chem. Eur. J.* **2020**, 26, 6879-6886
[2] Turnbull. D, Wetmore. S. D, Gerken. M, *Angew. Chem.* **2019**, *58 (37), 13035-13038*

New Synthetic Routes for Arylxenonium(II) Salts and Study of Their Lewis Acidity

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Since the first Xe−C bond was reported in 1989,[1] the number of organoxenon compounds has raised significantly.[2] Nevertheless, obtaining these compounds requires complex setups and severe reaction conditions. In order to make these species more accessible, by combining previous synthetic routes reported by Frohn and Naumann,[2] our new synthetic approach comes into play (Scheme 1). This new route allowed us to acquire a plethora of arylxenonium(II) salts in milder conditions and in moderate to high yields.

$$\mathrm{K[RBF_3]} + \mathrm{BF_3{\cdot}OEt_2} \xrightarrow[-\mathrm{K[BF_4]}]{\mathrm{CH_2Cl_2}} \mathrm{RBF_2{\cdot}OEt_2} \xrightarrow{\mathrm{XeF_2}} \mathbf{[RXe][BF_4]}$$

Scheme 1. Synthetic route for arylxenonium(II) salts (R = fluorinated aryl group).

In recent years the search for Lewis acids of main group elements has been of increasing interest, yet Group 18 has remained unexplored. In fact, within the family of cationic Lewis acids, the acidic properties of xenonium(II) ions have not yet been investigated.[3] Herein we display the first Lewis acidity study of arylxenonium(II) compounds $[RXe]^+$ (R = fluorinated aryl group), by theoretical (Fluoride Ion Affinities) and experimental methods (Gutmann-Beckett adducts). We hope this expands the applications of organoxenon compounds.

References

[1] a) Frohn, H. J.; Jakobs, S. J. *Chem. Soc., Chem. Commun.,* **1989**, 625-627. b) Naumann, D.; Tyrra, W. J. *Chem. Soc., Chem. Commun.,* **1989**, 47-50.

[2] Frohn, H.-J.; Bardin, V. V. *Organometallics,* **2001**, *20 (23),* 4750-4762.

[3] Erdmann, P.; Schmitt, M.; Sigmund, L. M.; Krämer, F.; Breher, F.; Greb, L. *Angew. Chem. Int. Ed.,* **2024**, *63 (22),* e202403356.

Platinum-Catalysed Hydrofluorination of Alkynes Promoted by a Fluoride Shuttle

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Fluoroalkenes have gained interest as a bioisoster of amide functional groups.[1,2] An efficient synthetic route to incorporate these fluorinated motifs involves the hydrofluorination of alkynes.[3] Previously we reported on the development of a platinum-catalysed process for the hydrofluorination of alkynes.[4] Herewith, we describe a hydrofluorination reaction of internal alkynes catalysed by Pt(II) dichlorido complexes conducted at room temperature. Various Pt(II) dichlorido complexes bearing chelating phosphines were synthesised and studied towards their catalytic behaviour. Mechanistic investigations suggest the involvement of a dicationic Pt(II) bisalkyne as well as a cationic *ß*-fluorovinyl Pt(II) complex in the catalytic cycle. The hydrofluorination is enabled by a nucleophilic attack of a perfluorinated anion at the electrophilic alkyne ligand of the dicationic Pt(II) complex demonstrating the ability of BF_3, HF as well as PF_5 to act as a fluoride shuttle, which is also supported by DFT calculations. The catalytic hydrofluorination system can be applied to a wide substrate scope to generate fluoroalkenes bearing bulky alkyl, aryl and electron withdrawing groups, such as ester and carbonyl substituents.

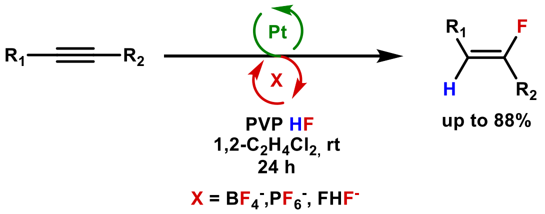

Figure 1. Platinum-catalysed hydrofluorination of alkynes promoted by a fluoride shuttle.

References

[1] Kumari, S.; Carmona, A. V.; Tiwari, A. K.; Trippier, P. C. *J. Med. Chem.,* **2020**, *63*, 12290-12358.
[2] Altman, R. A.; Sharma, K. K.; Rajewski, L. G.; Toren, P. C.; Baltezor, M. J.; Pal, M.; Karad, S. N. *ACS Chem. Neurosci.,* **2018**, *9*, 1735-1742.
[3] Gauthier, R.; Paquin, J. F. *Eur. J. Chem.,* **2023**, e202301896.
[4] Sander, S.; Braun, T. *Angew. Chem. Int. Ed.,* **2022**, *61,* e202204678.

C–F bond Activation of Fluoroalkanes *via* Germylium Ions Catalysis

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In the last decades, metal-free C–F bond activation with main group compounds have gained attention, and compounds showing a strong Lewis-acidity are of particular interest.[1,2] Group 14 compounds are known to be good Lewis-acids and the Braun group started to explore the properties and reactivity of germylium systems towards C–F[3] and C=C[4] bonds.

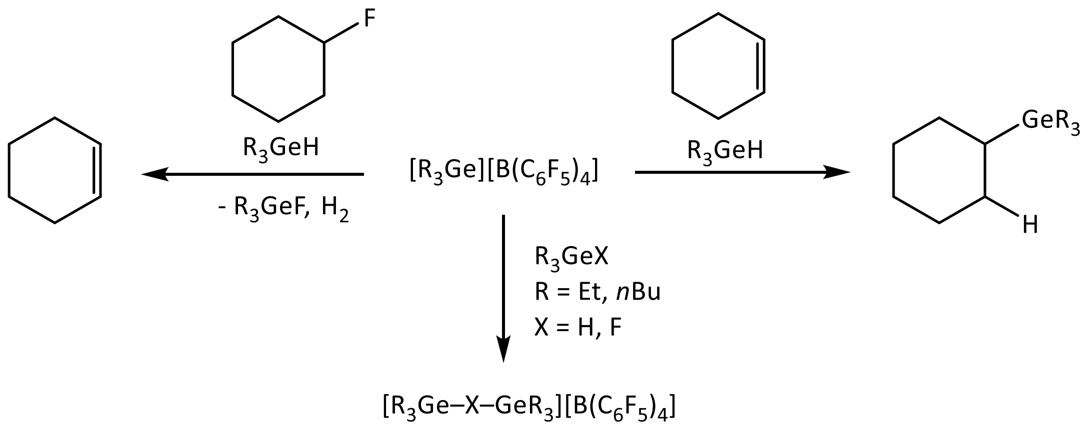

Figure 1. Reactivity of germylium ions with fluorocyclohexane, cyclohexene and other germane species.

Germylium ions $[R_3Ge][B(C_6F_5)_4]$ stabilized by a weakly coordinating anion could be isolated and reacted to further cationic derivatives (see **Figure 1.**). Their properties and reactivity were investigated and the germylium ions/germane system revealed an interesting reactivity towards the C–F bond activation of mono- and polyfluoroalkanes leading to the formation of dehydrofluorinated products, whereas reactions using *in situ* generated or isolated silylium ions exclusively lead to hydrodefluorinated products.[5,6] Moreover hydrogermylation of alkenes and alkynes using this same system has also been observed, opening up a new range of possibilities for the functionalisation of these substrates.

References

[1] Stahl, T.; Klare, H. F. T.; Oestereich, M. *ASC Catal.*, **2013**, 3, 1578−1587.
[2] Pei, R.; Chang, W.; He, L.; Wang, T.; Zhao, Y.; Liang, Y.; Wang, X. *Nat. Commun.,* **2024**, 15, 7943.
[3] Talavera, M.; Meißner, G.; Rachor, S.; Braun, T. *Chem. Comm.,* **2020**, 56, 4452–4455.
[4] Meißner, G.; Kretschmar, K.; Braun, T. *Angew. Chem. Int. Ed.,* **2017**, 56, 16338 –16341.
[5] Scott, V. J.; Celenligil-Cetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.*, **2005**, 127, 2852–2853.
[6] Douvris, C.; Stoyanov, E. S.; Tham, F. S.; Reed, C. A. *Chem. Comm.,* **2007**, 1145–1147.

Increasing the Oxidation Strength of Polynitrile Oxidizers by Coordination to Lewis Acids and Synthesis of a new strong Lewis Acid

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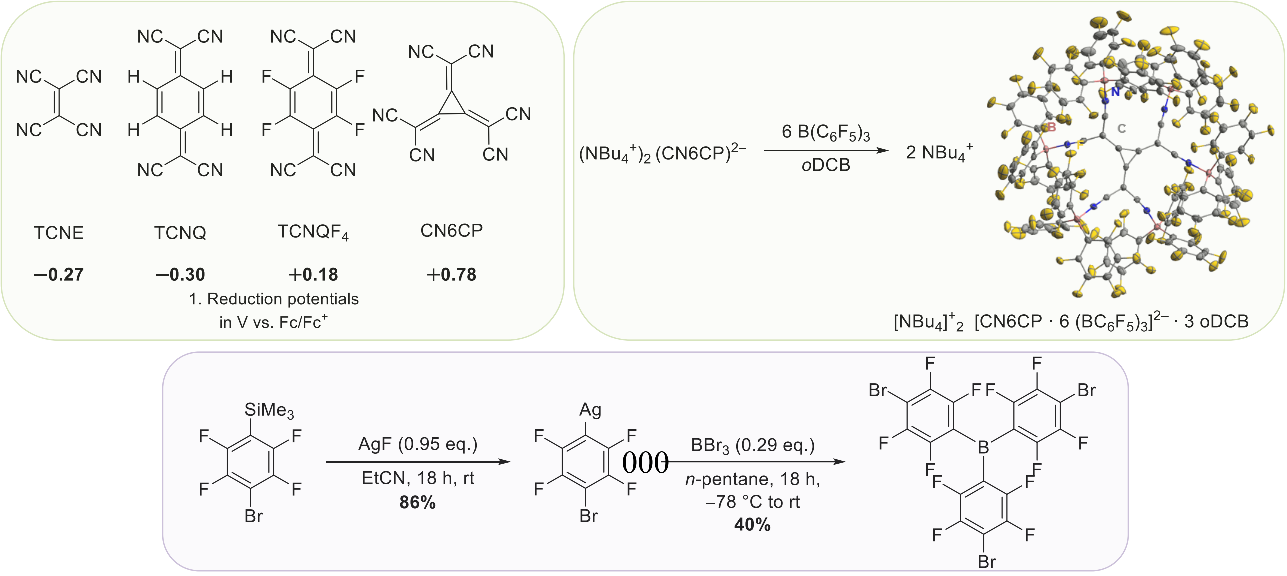
Organic polynitriles with conjugated π-systems, like TCNQ(F$_4$) or CN6CP are mild to strong oxidizers and are widely used as p-dopants for organic semiconductors (Scheme 1, left). Previous studies from our group have shown, that treating such nitriles with the strong Lewis acid B(C$_6$F$_5$)$_3$ leads to a coordination of all nitrile groups to the Lewis acid, significantly increasing the oxidation strength by approximately 1.0 V.[1]
Currently, further oxidation-systems [TCNQF$_4$ · 4 B(C$_6$F$_5$)$_3$] and [CN6CP · 6 B(C$_6$F$_5$)$_3$] are under investigation, which offer even higher oxidation strengths by coordination to the Lewis acid (Scheme 1, right).



Scheme 1. Examples of polynitriles oxidizers (left), the oxidation system [CN6CP · 6 B(C$_6$F$_5$)$_3$] (right) and the synthesis of B(C$_6$F$_4$Br)$_3$.

Since both the crystallization and the *sc*XRD-analysis of these adducts has proven challenging, we aimed to synthesize the strong Lewis acid B(C$_6$F$_4$Br)$_3$. The presence of heavier atoms was expected to facilitate XRD-measurements. The synthesis was successfully carried out in three steps starting from C$_6$F$_4$Br$_2$ via silylation, transmetalation to silver, and finally transmetalation to boron (Scheme 1, bottom). The Lewis acidity was determined through both, experimental and theoretical methods, revealing a slightly increased acidity in comparison to commercially available B(C$_6$F$_5$)$_3$.

References

[1] P. A. Albrecht, S. M. Rupf, M. Sellin, J. Schlögl, S. Riedel, M. Malischewski, *Chem. Commun.* **2022**, *58*, 4958–4961.

Silver Fluorides in Mixed Oxidation States (I)/(II)

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Fluorine compounds with metals have been used since ancient times when various civilizations utilized fluorite (CaF_2) for the production of vessels. Today, these compounds find applications in fields such as energy production and storage, catalysis, metallurgy, and microelectronics [1].
Silver fluorides with mixed oxidation states of $Ag^{(I)}/Ag^{(II)}$ are of particular interest, as it is predicted that compounds containing flat $[AgF_2]$ sheets doped with Ag(I) could exhibit high-temperature superconductivity. Such properties would enable the development of modern, lossless power transmission lines [2].
So far, silver fluorides with mixed oxidation states have only been known for silver(II)/(III) compounds, such as Ag_2F_5 and Ag_3F_8. These compounds have been thoroughly described and characterized, as previously reviewed [2]. The goal of this work was to synthesize and characterize new compounds: $Ag^{(I)}Ag^{(II)}F_3$ and $Ag^{(I)}_2Ag^{(II)}F_4$, which constitute the first silver(I)/(II) fluorides. They were obtained by direct synthesis from silver(I) fluoride and silver(II) fluoride at elevated temperatures in an atmosphere of gaseous argon.
The characterization of the obtained compounds included X-ray diffraction measurements, based on which the indexing of reflections for the new phases was performed. From the unit cell parameters obtained in the indexing process, structures were identified and then refined using the Rietveld method. For the $AgAgF_3$ compound, an orthorhombic unit cell with space group *P*mcn was determined, while for Ag_2AgF_4, a monoclinic unit cell with space group $P2_1/c$ was identified. Further characterization included Raman spectra measurements, which were compared with theoretical calculations. Magnetic and electronic properties were also studied theoretically [3].
Simultaneously, another research team successfully obtained the same compounds albeit $AgAgF_3$ was prepared in a different polymorphic form than the one reported here [4].

References

[1] Cochet-Muchy, B.; Portier, J. Inorg. Solid Fluorides, In: Hagenmuller, P., Ed.; Academic Press, **1985**, 565–605, ISBN: 978-0-12-313370-0.
[2] Grochala, W.; Hoffmann, R. Angew. Chem. Int. Ed., **2001**, 40, 2742–2781.
[3] Kuder, K.; Koteras, K.; Mazej, Z.; Grochala, W. https://arxiv.org/abs/2408.10753 (**2024**).
[4] Belak Vivod, M.; Jagličić, Z.; King, G.; Hansen, T. C.; Lozinšek, M.; Dragomir, M. J. Am. Chem. Soc., **2024**, 146, 30510–30517.

Bioorganic & Medicinal Chemistry

How does Fluorine Really Affect the Performance of Pharmaceuticals?

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At a meeting like this we are all very well aware of the beneficial effects fluorine can have on the properties of pharmaceuticals. This poster will use a combination of cheminformatics, statistical analysis and real examples to better understand how fluorine really compares to the performance of other common functional groups.

A **molecular matched pair analysis** has been used to understand the effects of fluorine and a range of other functional groups on pharmaceutical properties including binding constants,[1] lipophilicity,[2] solubility, bioavailability and metabolism to see where fluorine's advantages really lie.

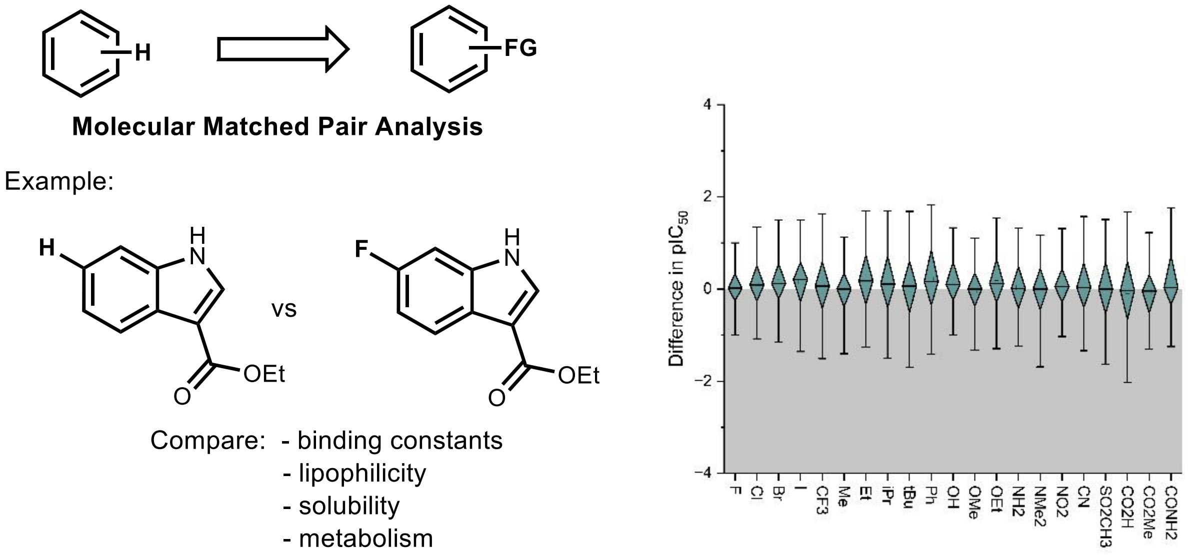

Figure 1. Process of Molecular Matched Pair Analysis and comparison of binding constants for various functional groups

References

[1] C.J. Summerfield, G. Pattison, unpublished results
[2] R.J. Glyn, G. Pattison*, *J. Med. Chem.* **2021,** *64,* 10246–10259

Surface Enhanced Infrared Absorption Spectroscopy on the Interaction of Cell Penetrating Peptides with Lipid Bilayers

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Cell-penetrating peptides (CPPs) are small chains of amino acids that can efficiently cross cell membranes, enabling the transportation of several therapeutic molecules such as drugs and genetic material into cells. Their extensive utility in drug delivery, gene therapy, and imaging positions CPPs as valuable tools for improving biomedical treatments [1]. Nevertheless, despite their wide-ranging use for delivering intracellular cargo, the particular mechanisms by which CPPs interact with cell membranes remain unclear. In order to shed light on this topic, we have earlier applied Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS) for the mechanism of peptide-lipid interactions between the CPPs (consisted as decaarginine, R10) with alkyl or perfluorinated tags and the solid-supported lipid bilayer (1-palmitoyl-2-oleoyl-glycero-3-phosphocholine, POPC), and observed the discrepancies for the interaction of CPPs with alkyl tag versus with perfluoroalkyl tag over POPC lipid bilayer [2]. To gain further insights into the interactions between the peptides and lipid bilayer, an orthogonal cyano tag (4-cyanobenzamide) was incorporated at different positions along the CPPs, accompanying the perfluoroalkyl tag. Moreover, SEIRAS measurements were also utilized on cyano-tagged CPPs loaded with the mCherry protein as a cargo molecule in the presence of a lipid bilayer, demonstrating the potential of this technique for studying molecular delivery systems. We expect this research to contribute to a profounder understanding of the mechanism for peptide-lipid interactions in the context of peptide-based intracellular delivery methods.

References

[1] Xie, J.; Bi, Y.; Zhang, H.; Dong, S.; Teng, L.; Lee, R. J.; Yang, Z. *Front. Pharmacol.* 2020, *11*, 697.

[2] Kozuch, J.; Ataka, K.; Heberle, J. *Nat. Rev. Methods Primers* **2023**, *3*, 70.

Investigating the Site-Specific Impact of Fluorine Substitution on Aromatic Interactions in a Tryptophan Zipper Peptide

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Fluorinated analogues of tryptophan (Trp) have found broad application as biocompatible NMR probes given fluorine's high sensitivity, broad chemical shift range, and its absence from biological systems[1,2]. While fluorine only minimally perturbs the molecular geometry of the Trp side chain, global implications are difficult to predict as they are highly regiospecific especially upon substitution of multiple Trp residues across a whole biological organism.[3,4] Herein we present a systematic study of the effect of fluoro-Trp substitution on the pairwise *edge-to-face* π-stacking interaction in the 12-residue β-hairpin peptide Trpzip2.[5] We employed a library approach to assess the regiospecific impact of all monofluorinated Trp derivatives on peptide structure and stability using circular dichroism (CD) and NMR. Global hairpin stability was improved or compromised upon site-selective incorporation of a single monofluoro-Trp regioisomer. Fluorine substitution revealed key CH/π contributions within the Trp/Trp packing, which could be fine-tuned based on the aryl-fluorine substitution pattern.

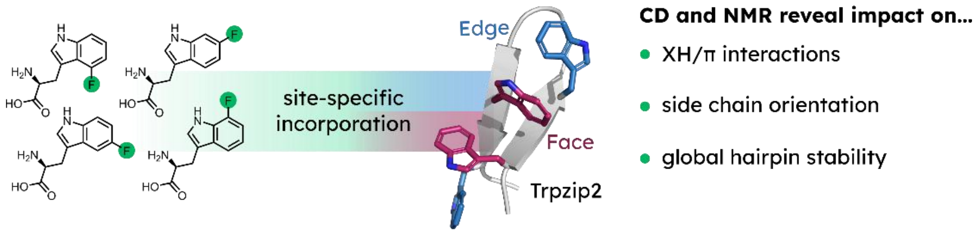

Figure 1. Graphical abstract. Analogues of the β-hairpin peptide Trpzip2 containing monofluoro-Trp regioisomers were chemically synthesized and studied by CD and NMR to evaluate the impact of fluorine-substitution on the *edge-to-face* Trp/Trp interaction.

References

[1] H. Qianzhu, E. H. Abdelkader, G. Otting, T. Huber, *J. Am. Chem. Soc.* **2024**, *146*, 19, 13641–13650.
[2] H. Welte, T. Zhou, X. Mihajlenko, O. Mayans, M. Kovermann, *Sci. Rep.* **2020**, *10*, 2640.
[3] F. Agostini, L. Sinn, D. Petras, C. J. Schipp, V. Kubyshkin, …, B. Koksch, *ACS Cent. Sci.* **2021**, *7*, 81–92.
[4] C. Treiber-Kleinke, A. A. Berger, L. Adrian, N. Budisa, B. Koksch, *Front. Synth. Biol.* **2024**, *1*, 1345634.
[5] A. G. Cochran, N. J. Skelton, M. A. Starovasnik, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 5578–5583.

Materials

Post-Metal-Etch HF Conditioning of BCAT Gate Oxide for Simultaneous GIDL Suppression and Word-Line Resistance Recovery in Sub-10 nm DRAM

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Refresh-driven failures have emerged as the dominant reliability and power bottleneck in sub-10-nm DRAM: gate-induced drain leakage (GIDL) now governs the tail of the retention-time distribution [1], while the ever-shorter retention times of nanoscale cells forces refresh activity that already accounts for ~25–27 % of total DRAM energy [2]. The problem is magnified in AI/HPC server DIMMs, where high-capacity devices operate at elevated temperature and utilization; industry road-maps therefore prioritize refresh-power cuts, as illustrated by the latest 10-nm-class DDR5 parts announced for data-centre workloads [3]. Current DRAM cells mitigate GIDL by adopting a **dual-work-function gate stack,** in which a high-Φ metal pad is locally overlaid on the conventional poly-Si gate. By **tuning the metal-to-poly overlap length,** engineers can raise the effective gate work function at the drain edge and thus suppress the high-field band-to-band tunnelling that drives GIDL. However, enlarging this overlap unavoidably inserts a long, narrow metal segment in series with the polysilicon word-line; the added interface contact resistance and current crowding increase gate-line RC delay and widen resistance distributions, creating a direct reliability–performance trade-off. To simultaneously suppress GIDL and restore word-line resistance margins, this study introduces a **post-metal-etch hydrofluoric-acid (HF) surface-conditioning step** that selectively strips etch-induced damage and residual metallic by-products from the BCAT trench sidewalls and gate-oxide interface. The restored interface integrity lowers trap density, reduces GIDL current, and tightens resistance distributions, all without incurring any cell-area penalty.

References

[1] Saino, K.; *et al.* Impact of Gate-Induced Drain Leakage Current on the Tail Distribution of DRAM Data Retention Time. *IEDM Tech. Dig.*, 2000, 33.4.1–33.4.4.
[2] Wang, S.-H.; Liang, Y.; Yu, C.-Y. Retention-Aware DRAM Auto-Refresh Scheme for Energy and Performance Efficiency. *Micromachines*, 2019, 10 (9), 590.
[3] Patel, D.; McGill, A.; Cutress, I. The Memory Wall: Past, Present, and Future of DRAM. *SemiAnalysis* (online), 2024.

Fluorine Gas Generation with Metal Fluoride Reduction

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Fluorine gas is industrially important, including in the utilization in enrichment of UF_6 in the nuclear industry and in semiconductor cleaning. The current industrial method for the production of fluorine gas is the electrolysis of HF in a KF-2HF molten salt (melting point: 71.7 °C) at an operating temperature around 90 °C and the fluorine gas produced is collected at the anode (Figure 1a).[1] On the other hand, there is a strong need for the development of a safe and small-scale on-site fluorine gas supply system in some academic and industrial spots. Nevertheless, it is difficult to miniaturize the industrial methods of fluorine gas production. Fluorine gas generation by electrolysis of metal fluoride in CsF-2.45HF room-temperature molten salt (melting point: 16.9 °C) was proposed for the small-scale use.[2] In this system, the cathodic reaction is the reduction of metal fluoride to metal without generating H_2 gas, which improves the safety of the electrolytic cell. Figure 1b shows a schematic diagram of the electrolytic cell using CuF_2 as metal fluoride. This cell has succeeded in producing high-purity fluorine gas (99%) [2]. Figure 1c shows a schematic diagram of the electrolytic cell with a solid-state fluoride ion conductor to separate the cathode and anode rooms. This design can enable the use of metal fluorides which can be oxidized at the anode and the redox behaviour of SnF_2 is presented as an example of this cell.

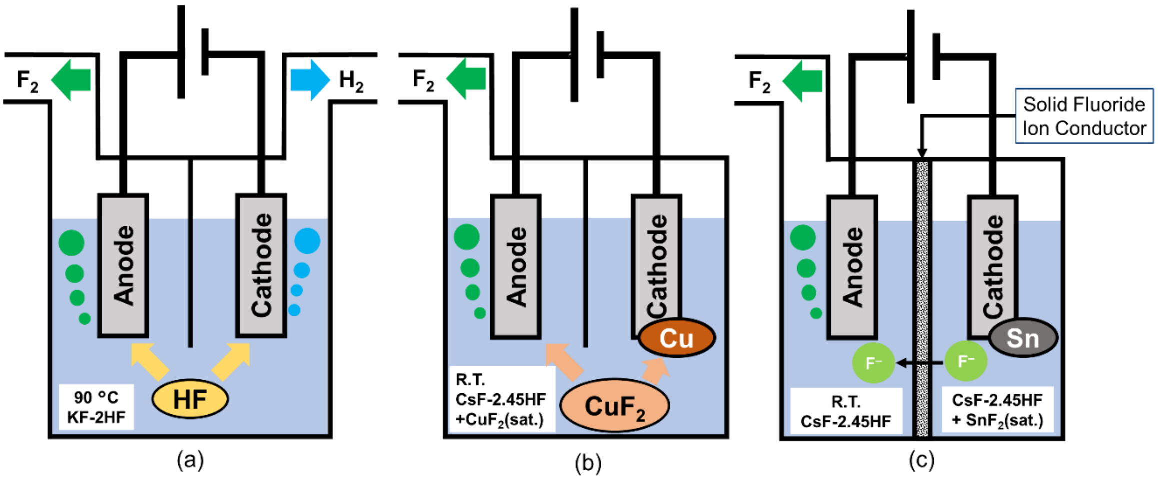

Figure 1. Schematic drawings of fluorine gas generators. (a) A conventional electrolysis method using the KF-2HF electrolyte, (b) the electrolysis method using the CsF-2.45HF molten salt containing CuF_2, and (c) the electrolysis method using the solid-state fluoride ion conductor and CsF-2.45HF molten salt containing SnF_2.

References

[1] H. Groult, *J. Fluorine Chem.* **119** (2003) 173–189.

[2] Matsumoto, K. Shima, T. Sugimoto, T. Inoue, R. Hagiwara, *Angew. Chem. Int. Ed.* **60** (2021) 7887–7892

Functionalization of Nanodiamonds with Perfluoropolyether Peroxide *Via* a Facile Thermochemical Process

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The functionalization of nanodiamonds (NDs) and fluorinated nanodiamonds (F-NDs) with perfluoropolyether (PFPE) peroxide was achieved through a thermal process, enhancing their surface properties. Fourier-transform infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance (NMR) spectroscopy confirmed the successful attachment of PFPE moieties, while X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) quantified the degree of functionalization. Water contact angle measurements demonstrated a significant increase in hydrophobicity compared to pristine materials, showing superhydrophobic behaviour on F-NDs. These findings provide valuable insights into the surface chemistry of PFPE-functionalized nanodiamonds and highlight their potential for application in systems requiring extreme hydrophobicity and enhanced chemical resistance.

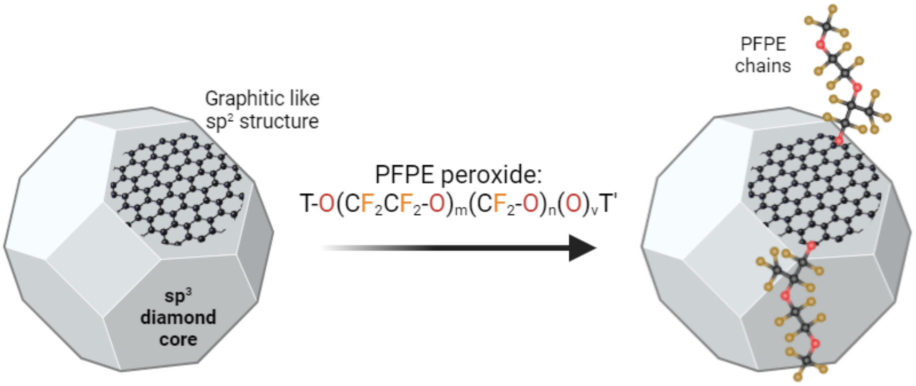

Figure 1. Nanodiamonds functionalization with perfluoropolyether peroxide graphical representation.

References

[1] Ceriotti, D., Marziani, P., Magagnin, L., Sansotera, M., Petit, E., Hajjar-Garreau, S., Dubois, M. Functionalization of Nanodiamonds with Perfluoropolyether Peroxide Via a Facile Thermochemical Process. Available at SSRN 493884 [*Submitted, under peer review*]

Mechanochemical Synthesis of Fluorinated Perovskites $KCuF_3$ and $KNiF_3$

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In this study two fluorinated perovskites, $KCuF_3$ and $KNiF_3$, were synthesized *via* solvent-free mechanochemical route, offering a sustainable alternative to conventional solvothermal methods. Perovskites are a class of semiconducting materials with tenable bandgaps, high charge-carrier mobilities, and long carrier diffusion lengths. The mechanochemical synthesis was optimized by refining the milling time at constant rotational speed. After 6 hours of milling, the target crystalline phases of $KCuF_3$ and $KNiF_3$ were obtained. Extended milling durations led to the formation of secondary crystalline phases, identified as K_2CuF_4 and K_2NiF_4. Comprehensive characterization using X-ray Diffraction, X-ray Photoelectron Spectroscopy, and Scanning Electron Microscopy confirm the selective formation of the desired fluorinated perovskites. The mechanochemical approach, compared with a novel mild solvothermal method, reveals promising results, highlighting solvent-free mechanochemistry as a powerful strategy in crystal engineering, able to simplify the synthesis procedures, lowering the use of hazardeous solvents and energy demands.

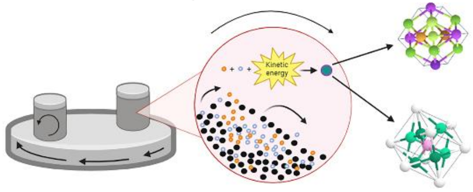

Figure 1. Graphical illustration of the synthetic process.

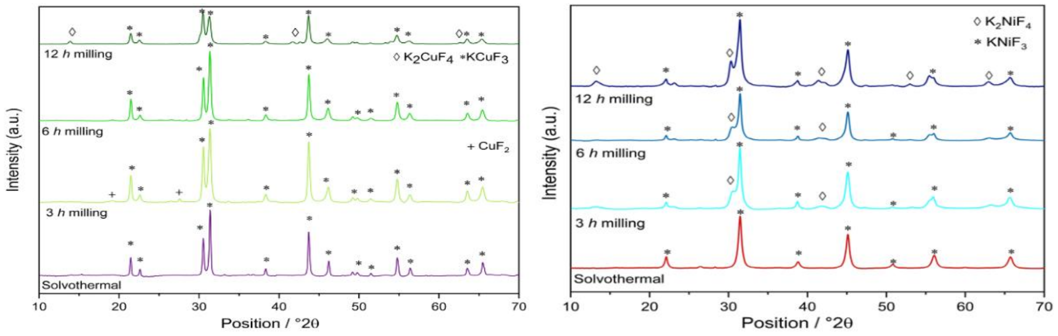

Figure 2. XRD patterns of the two fluorinated perovskites, $KCuF_3$ and $KNiF_3$.

References

D. Ceriotti, P. Marziani, F.M. Scesa, A. Collorà, C.L. Bianchi, L. Magagnin, M. Sansotera, RSC Mechanochem., **2024**, 1, 520–530.

Investigation of Dicationic Ionic Liquids with Difluorophosphate Anion

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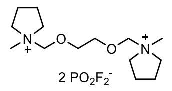
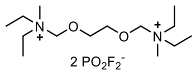
Recently, dicationic ionic liquids (DILs) have gained attention as electrolytes in secondary batteries. Compared to conventional monocationic ionic liquids (MILs), DILs can exhibit enhanced thermal stability and a broader electrochemical window. However, the larger molecular size and double charge of the cation tend to increase viscosity and melting point of the DILs, which can impact their practical application. Viscosity is a particularly critical factor for electrolytes, as lower viscosity is related to ionic conductivity and cell fabrication. Previous studies on piperidinium-based MILs have shown that introduction of the ether linker structure effectively reduces viscosity. [1]

Ionic liquids with difluorophosphate anion ($PO_2F_2^-$) were synthesized and characterized in a previous study. [2] In addition to low melting point and viscosity, $PO_2F_2^-$-based ionic liquids provide a high polarity owing to the large dipole moment on the anion.

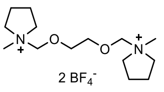
This study explores the introduction of the oxygen into the linker of the dication in addition to the incorporation of $PO_2F_2^-$ in order to obtain DILs with low melting point and viscosity. The resulting physical properties are compared with the physical properties of those with other fluorocomplex anions. (**Figure 1**)



$[C_{1O2O1}\text{-}(C_1Pyrr)_2][PO_2F_2]_2$



$[C_{1O2O1}\text{-}(N_{221})_2][PO_2F_2]_2$



$[C_{1O2O1}\text{-}(C_1Pyrr)_2][BF_4]_2$

	T_g/ °C	ρ/ g cm−3	η/ mPa s	σ/ mS cm−1	EW/ V
$[C_{1O2O1}\text{-}(C_1Pyrr)_2][PO_2F_2]_2$	−73	1.349	2000	0.42	4.91
$[C_{1O2O1}\text{-}(N_{221})_2][PO_2F_2]_2$	−68	1.277	3700	0.22	4.27
$[C_{1O2O1}\text{-}(C_1Pyrr)_2][BF_4]_2$	−49	1.305	11900	0.13	4.91

Figure 1. Structures and physical properties of dicationic ionic liquids.

References

[1] T. Nokami, T. Yamashita, T. Komura, N. Handa, M. Shimizu, K. Yamaguchi, Y. Domi, H. Usui, H. Sakaguchi, and T. Itoh, *Faraday Discuss*., 2018, 206, 523.
[2] K. Matsumoto, R. Hagiwara, Inorg. Chem., 2009, 48, 7350.

Activated Carbon for PFAS and Pharmaceutical Removal: A Sustainable Water Purification Approach

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The increasing presence of contaminants of emerging concern (CECs), such as per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals, in environmental waters has raised significant concerns due to their persistence and potential toxicity. Traditional water treatment methods highlight the need for innovative solutions. Activated carbons (AC) have emerged as a promising adsorbent for the removal of CECs, owing to their high surface area and adsorption capacity.[1] However, the sustainability of AC production and its cost-effectiveness remain key challenges, especially when considering the environmental impact of its sourcing. This work focuses on characterizing the adsorption capacity of AC derived from biomass waste as part of a circular economy approach. The biomass is reused into activated carbon and its ability to adsorb PFAS and pharmaceutical contaminants from aqueous solutions is evaluated. Several parameters, such as adsorption kinetics, equilibrium, and capacity, are assessed under different conditions to determine the effectiveness of AC in removing these pollutants. The results demonstrated significant potential for removing CECs, including PFAS and pharmaceuticals, from environmental water. This approach not only offers a sustainable method for waste valorisation through circular economy principles but also provides an effective solution for tackling persistent water contamination. The promising adsorption capacity of biomass-based AC offers a pathway for more sustainable, cost-effective water treatment strategies.

References

[1] Mokhati, A., Benturki, O., Benturki, A., Fennouh, R., Kecira, Z., Bernardo, M., Matos, I., Lapa, N., Ventura, M., Soares, O. S. G. P., Rego, A. M. B. D., & Fonseca, I. Applied Sciences, 2022, 12(15), 7607.

Sustainable Water Treatment: Regenerating Activated Carbon to Remove Emerging Contaminants

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The persistence of contaminants of emerging concern (CECs), such as per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals, in environmental water matrices, like surface water and groundwater, presents significant challenges to both the environment and public health. Due to their resistance to conventional treatment methods, these CECs can accumulate over time, posing long-term toxicity risks. This work will investigate the ecotoxicity of these CECs using multicellular organisms, such as Daphnia magna, to highlight the potential risks they pose to aquatic organisms and ecosystems, even at low concentrations.[1] Additionally, the regeneration of activated carbons using greener solvents, such as ionic liquids and eutectic systems, will be explored as a sustainable alternative to conventional ethanol and methanol solvents.[2] The effectiveness of these environmentally friendly solvents in restoring the adsorptive capacity of activated carbon for removing PFAS and pharmaceutical contaminants will be evaluated. By combining greener regeneration methods with an understanding of CECs toxicity, this work will provide valuable insights into more sustainable and effective strategies for mitigating persistent water contamination while minimizing ecological risks.

References

[1] Reilly, K., Ellis, L. A., Davoudi, H. H., Supian, S., Maia, M. T., Silva, G. H., Guo, Z., Martinez, D. S. T., & Lynch, I. *Frontiers in Toxicology*, 2023, *5*.

[2] Mokhati, A., Benturki, O., Benturki, A., Fennouh, R., Kecira, Z., Bernardo, M., Matos, I., Lapa, N., Ventura, M., Soares, O. S. G. P., Rego, A. M. B. D., & Fonseca, I. *Applied Sciences*, 2022, *12*(15), 7607.

Lewis-acid Mediated Mechanochemical Degradation of PVDF

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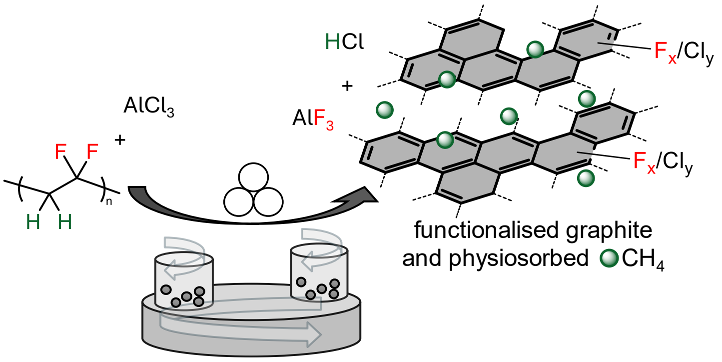
Polyvinylidene fluoride (-$[CH_2CF_2]_n$-, PVDF) waste, characterized by its recalcitrant nature and extensive applications, poses a significant environmental challenge.[1] This research explores a mechanochemical approach for the sustainable valorization of PVDF, utilizing ball milling with anhydrous $AlCl_3$ to achieve quantitative mineralization. The process results in the generation of AlF_3 and functionalized graphite, along with gaseous byproducts (HCl and CH_4). The mechanistic pathway involves as key steps Lewis acid-catalyzed C–F bond activation, followed by dehydrofluorination and aromatization. The method provides an effective solution for PVDF waste management, enabling the production of high-value materials from polymer waste streams. The findings contribute to the development of sustainable practices for polymer recycling and resource recovery, addressing the environmental concerns associated with fluoropolymer disposal.



Scheme 1. General scheme for PVDF degradation by mechanochemical treatment.

References

[1] a) Stoiber, T.; Evans, S.; Naidenko, O. V. *Chemosphere* **2020**, *260*, 127659; b) Garg, S.; Kumar, P.; Mishra, V.; Guijt, R.; Singh, P.; Dumée, L. F.; Sharma, R. S. *J. Water Process Eng.* **2020**, *38*, 101683.

Oxidative Fluorination of Cu/ZnO Methanol Catalysts with NF_3 as Fluorinating Agent

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Global warming and moving away from fossil fuels as raw materials demand a reorganization of the energy carrier portfolio. Copper and zinc oxide (Cu/ZnO) catalysts[1] are known to convert the greenhouse gas CO_2 together with hydrogen (H_2) into the platform chemical methanol (MeOH).[2] In the research group of Prof. Krossing, oxidative fluorination is utilized to enhance catalyst activity for methanol synthesis from CO_2 and H_2.[3] The aim is to find a fluorinating agent that is safe to handle in a production system and for the user.
A device was set up to create fluorinated catalysts using the inert NF_3 as a fluorinating agent. Catalysts were activated with H_2 and fed with CO_2 and 3 H_2 at 230-250 °C and 40 bar. Gas chromatography quantified the catalytic products, and the feed gas composition was varied between CO/2 H_2 and CO_2/3 H_2 to assess catalyst compatibility.
The catalysis results show comparable catalysis results can be achieved with the fluorinating agent NF_3 (*c.f.* F_2 systems[3]), which is new for catalysts and can show a significant increase in activity compared to the untreated Cu/ZnO catalyst. The productivity of the MeOH is increased, and the selectivity of the MeOH and the CO_2 conversion is also improved. It should also be noted that lowering the catalysis temperature by 20 °C achieves the same MeOH productivity as the untreated catalyst at 250 °C.

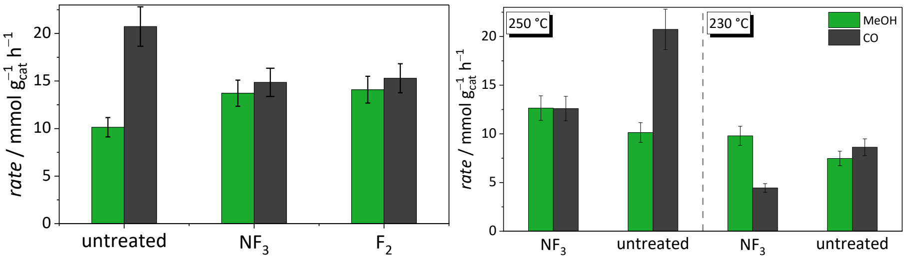

Figure 1. Catalytic testing of 100 mg Catalysts at 250 °C (230 °C), 40 bar and $CO_2 : H_2 = 1 : 3$, 33 mL min^{-1}. Left) Comparison of two different fluorinated catalysts with untreated Cu/ZnO catalyst. Right) Comparison of the activity at various temperatures with the untreated catalyst.

References

[1] H.Y. Chen, S.P. Lau, L. Chen, J. Lin, C.H.A. Huan, K.L. Tan, J.S. Pan, *Appl. Surf. Sci.* **1999**, 152, 193-199.
[2] X. Zhang, G. Zhang, C. Song, X. Guo*, Front. Energy Res.* **2021**, 8, 621119.
[3] a) S. M. Fehr, K. Nguyen, C. Njel, I. Krossing, *ACS Catal.* **2021**, *11*, 13223; b) S. M. Fehr, K. Nguyen, C. Njel, I. Krossing, *ChemCatChem.* **2022**, *14*, e202101500; c) L. D. Ernst, C. Njel, W. Marquart, S. Raseale, M. Claeys, N. Fischer, I. Krossing, *ACS Catal.*, **2024**, *14*, 12199.

Fluorinated Hexosome Carriers for Enhanced Solubility of Drugs

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Designing nanomaterials for drug encapsulation is a crucial yet challenging aspect for pharmaceutical development. An important step is synthesizing amphiphiles that form stable supramolecular systems for efficient drug loading. In the case of fluorinated drugs, these have superior properties but also a tendency toward reduced water solubility. Fluorinated hexosome carriers are reported here for the first time. These are formed from non-ionic dendritic amphiphiles and encapsulate the fluorinated drug Leflunomide with high efficiency (62 ± 3%), increasing its solubility by 12-fold. Amphiphiles with varying tail groups (fluorinated/alkylated) are synthesized and their supramolecular self-assembly is investigated using cryogenic transmission electron microscopy and small-angle X-ray scattering. Furthermore, Leflunomide and its equivalent non-fluorinated counterpart are encapsulated within fluorinated and non-fluorinated assemblies. Self-assembly and encapsulation mechanisms are well supported by coarse-grained molecular simulations, yielding a fundamental understanding of the new systems. The fluorinated amphiphile is less cytotoxic to HeLa cells by a factor of more than 5 (up to 2.5 mg ml^{-1}) compared to the alkylated amphiphile.

References

[1] Rosati, M.; Acocella, A.; Pizzi, A.; Turtù,G.; Neri, G.; Demitri, N.; Raffaini, G.; Donnio, B.; Zerbetto, F.; Baldelli Bombelli, F.; Cavallo, G.; and Metrangolo, P. *Macromolecules*, **2022,** *55* (7), 2486-2496.
[2] Singh, A. K.; Schade, B.; Rosati, M.; Rashmi, R.; Dichiarante, V.; Cavallo, G.; Metrangolo, P.; Haag, R. *Macromol. Biosci.* **2022**, *22*, 2200108.

Perfluorocarbon Emissions During Dysprosium Electrolysis from Fluoride-Based Melts

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Current environmental policies demand that the entire electrolysis process of greening and cleaning be implemented, from metal extraction to material synthesis. Therefore, there is an urgent need to develop an advanced new green metal extraction process to meet the stringent environmental protection requirements [1]. In general, RE electrolysis generates unnecessarily high emissions of perfluorocarbon gases (PFCs), such as tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6), which are potent greenhouse gases and are not filtered or destroyed in the off-gas [2]. To address this issue, understanding of the micro-generation mechanism of the greenhouse gases (GHGs) in the Dy electrolysis is crucial in an effort to largely reduce the PFC emission and keep the process in the green process window. To apprehend the mechanism of the greenhouse gas formation CO, CO_2 and perfluorocarbon gases (CF_4 and C_2F_6), in-situ measurements of the chemical identity and amount of the anode gases during electrodeposition of dysprosium metal from fluoride-based melts DyF_3 – LiF = 50 – 50% with 1% Dy_2O_3 were performed.

In the electrolysis process at constant potentiostatic mode which leads to the electrodeposition of Dy metal from fluoride-based melts with a carbon anode and a molybdenum cathode PFC emission is involved as well. However, in the potential range where Dy^{3+} is reduced to Dy metal, the experimentally measured FTIR results from the on-line anode off-gas analysis indicate that the anode gas products mainly consist of CO and CO_2, while negligible amounts of CF_4 were recorded to have been evolved, and C_2F_6 has been detected just above or below the detection limit. The results showed that the CF_4 concentration was not higher than 0.1 ppm in the Dy electrolysis process. Fluorides and oxyfluoride complexes such as [REFx]y- and [REOFx]y- are probably formed during the dissolution of Dy_2O_3 in fluoride-containing melts. The complexes are involved in the reaction with the GC anode, and CO_2/CO and CF_4/C_2F_6 are formed depending on the working potential of the anode [3]. A comparison of the experimental results obtained from Dy_2O_3+DyF_3+LiF electrolyte has shown that the relatively low Dy deposition overpotential prevents fluorocarbon evolution at the anode. The approach presented here to the reduction of the PFC gases emission during RE electrolysis can be considered as an innovative method due to its positive impact on the environment.

Acknowledgements

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References

[1] C-Z. Z.; B. M.; S. A.E.; P. D.; F. S. A.; P. R. R. *Metals,* **2024,** *14*, p. 658.
[2] V. H.; F. B. J. Nonferrous Metall., **2017**, *6,* pp. 27–46.
[3] V. S. C.; N. M. P.; L. P.; D. F.; S. S. R.; B. F.; J. N. J. *Materials,* **2025**, *18,* p. 184.

CF_4/C_2F_6 Gases Emissions During Rare Earth Electrolysis

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Rare earth elements (REE) have become vital in our daily life because they are used as a key component in a variety of the advanced technology applications [1]. Large scale REE exploitation is a waste-generating process that causes serious environmental problems and forces industrialised countries to turn to alternative resources for RE, such as recycling of the elements from end-of-life (EOL) products [1]. Fluoride-based molten salts are widely used in the RE molten salt electrolysis (MSE) because of their distinct advantages such as continuous production and short process flow [2]. However, this electrolyte media is associated with the consumption of anode, and emission of greenhouse gases (GHGs), CO/CO_2 and perfluorocarbon gases (PFCs), mainly CF_4 and C_2F_6. Our work in this area has led to the development of a new process for the recovery of REE from EOL magnets. Pyrometallurgical treatment of spent NdFeB magnets was used to produce the magnet recycling derived oxides (MRDO), a REE containing product. The subsequent fluoride-based MSE of the produced MRDO was carried out to recover REE from EOL magnets [2,3]. Continuous monitoring of PFC emissions by in-situ FTIR-spectrometry during the RE recovery from NdFeB EOL magnets by MSE was the main objective of this study. The RE electrolysis from fluoride-based molten salts composed of NdF_3+PrF_3+LiF with MRDO was carried out using molybdenum (Mo) as a cathode, tungsten (W) as a reference electrode, and a glassy carbon (GC) electrode as an anode. The FTIR results show that the anode gas products were composed mainly of CO and CO_2, while CF_4 has been detected before the full anode effect and C_2F_6 at and after this phenomenon. The anode reactions in the fluoride-based melts after the dissolution of RE oxides are most likely the result of the oxide or fluoride complexes formed in the electrolyte, on whose very formation the subsequent reactions at the GC anode depend. The generated oxygen reacts with GC to produce CO and CO_2. Upon fluoride salt dissolution produced F^- ions, can also react with GC anode and generate PFC compounds such as CF_4 and C_2F_6. The content of CF_4 during constant potentiostatic electrolysis was on average 0.3 ppm except for spikes that were detected periodically, and then the highest concentration was around 1 ppm, while C_2F_6 was not detected.

Acknowledgements
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References
[1] L. B.; G. J.; Z. X.; Y. W.; R. M.; X. B.; H. H. *Molecules*, **2024,** *29*, p. 4624.
[2] C. H.; P. L.; S. S. R.; F. D.; C. V. S.; F. B. *Metals,* **2023**, *13*, p. 559,
[3] V. S. C.; N. M. P.; L. P.; D. F.; S. S. R.; B. F.; J. N. J. *Materials,* **2025**, *18,* p. 184.

Computational Chemistry

Understanding the Key Features Driving the Solubility Behavior of F-gases in Solvents through the SAFT-VR Mie Model for Refrigeration Applications

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Reducing the environmental impact of greenhouse gases (GHGs) in terms of their global warming potential (GWP) remains a major challenge, as their accumulation in the atmosphere is the primary cause of global warming. Fluorinated refrigerants, such as hydrofluorocarbons (HFCs) are significant emission sources, with hydrofluoroolefins (HFOs) emerging as a more eco-friendly alternative in terms of GWP. The recovery and recycling of fluorinated gases (F-gases) are key research areas to avoid further production of these compounds, contributing to circular economy approaches. While in recent years a variety of solvents of different nature have been proposed for the separation of F-gases, there is not a clear comparison between those solvents and its practical application in the recovery of commercial blends, such as R410A, R407F, R404C or R513A. In this context, it is crucial to understand the interactions arising according to the chemical structure of each fluid, as well as the impact of the polarity exerted by the fluorine atoms in the refrigerant.
In this contribution, a detailed and accurate theoretical model based on the Statistical Associating Fluid Theory with a Mie Intermolecular Potential (SAFT-VR Mie) [1] has been developed to describe the solubility of several fluorinated refrigerants (HFCs and HFOs) in different solvents. The selected solvents fall into three main categories: Ionic Liquids (ILs), Deep Eutectic Solvents (DESs), and biomass-derived components. All refrigerants were modeled as non-associating yet dipolar fluids, achieving an excellent description of vapor-liquid equilibrium, vapor pressure, and enthalpy of vaporization. On the other hand, solvents containing ring structures were modeled using an extended version of the SAFT-VR Mie equation, which includes descriptors for molecules with planar ring structures [2], allowing for a more realistic representation of their structure. A rational discussion about the impact associative and/or polar contributions between the F-gas and the solvent is considered based on their molecular conformation, as well as the inclusion of fluorine atoms in the solvent. Finally, the selectivity between gases conforming commercial blends will be predicted, so as to rank the preferential solvents for a potential separation unit.

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References

[1] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. Adjiman, E. Muller, G. Jackson, J. Chem. Phys 2013, 139, 154504.
[2] Müller, E. A., & Mejía, A. (2017). Extension of the SAFT-VR Mie EoS to model homonuclear rings and its parametrization based on the principle of corresponding states. Langmuir, 33(42), 11518-11529.

Investigating the Electronic Structure of Lanthanoid Trifluorides using X-Ray Spectroscopy and First Principle Methods

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Lanthanoid trifluorides (LnF3, Ln = Y, La-Lu) exhibit unique electronic properties relevant to optical and electronic applications. They crystallize in two different structures, whereas YF_3 and PmF_3-LuF_3 have space group Pnma, LaF_3, CeF_3, PrF_3 and NdF_3 crystallize in space group P-3c1. Due to a similar charge to ion radius ratio, YF_3 is considered a geochemical twin of HoF_3. In this study, we combine X-ray spectroscopical methods with first-principle density functional theory (DFT) calculations to investigate their electronic structure. Initial band gap measurements provide an experimental benchmark for computational validation. Using the Vienna Ab initio Simulation Package (VASP), we optimize experimentally measured crystal structures and perform calculations to determine the band structure and density of states. Due to the strongly correlated and relativistic nature of localized 4f electrons, accurate modeling of their contributions to the overall electronic structure remains a challenging task, which requires careful choice of corresponding functionals and other computational settings. We use small-core relativistic pseudotentials and +U corrections for GGA functionals and range separated hybrid functionals (HSE06) to evaluate their performance by comparison with experimental and previous literature results. [1][2] This combined experimental and theoretical approach eludicates the special electronic properties and clarifies the nature of the electronic excitations. The optical band gap of all systems is in the range of 8.4 to 9.5 eV and slightly increasing with atomic number. Recorded fluorescence yield XAS-spectra of SmF_3, EuF_3, HoF_3, ErF_3 and YbF_3 show a pre-edge peak which is consistent with occurence of localized f-band gap states in calculated density of states.

References

[1] J. Anders; N. Limberg; B. Paulus; *materials,* **2022**, *15*, 6048-6061.
[2] A. Oreshonkov et al.; *J. Phys. Condens. Matter*, **2018**, *30*, 255901.

The Bioinorganic Impact of Fluorine Studied by Vibrational Spectroscopy

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ATCUN peptides are histidine-containing tripeptides with metalloenzyme properties in their metal-bound form. For instance, their cobalt (Co) complexes have catalytic activity for hydrogen production and nitrite reduction. Here, we studied Co complexes of ATCUN peptides containing (non-)fluorinated amino acids. Four different residues (amino-acid side chains) were placed in positions R_1 and R_2 (Fig. 1 a). Using infrared (IR) and resonance Raman spectroscopy supported by DFT-based anharmonic frequency calculations, we examined the vibrational modes of the complexes to understand the impact of fluorination and lay a foundation for nonlinear IR experiments.

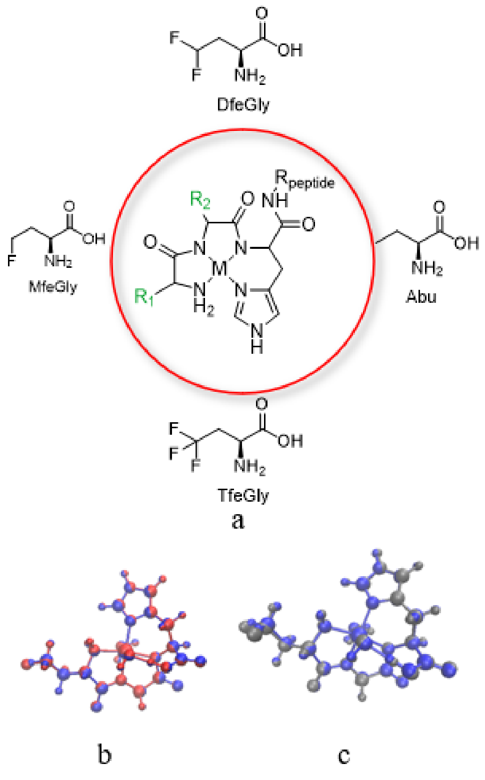

Figure 1. (a) Architecture of (fluorinated) ATCUN complexes. (b and c) Structural impact of mono- and difluorination.

C-F stretching vibrations are valuable markers for studying fluorination, expected in the 1100-1300 cm^{-1} region. However, IR spectra showed no significant differences between fluorinated and non-fluorinated complexes, and computational investigations revealed that these vibrations appear at unusually low frequencies <1000 cm^{-1}. We ascribe this observation to metal binding. Moreover, fluorine has a high electronegativity and hydrophobicity, which typically causes significant changes in the structures of peptides. We compared the computed structures and vibrational properties of monofluorinated (red; b) and difluorinated variants (grey; c) with the nonfluorinated analogue (blue; b & c). Surprisingly, structural and spectroscopic changes were negligible, which points towards a high rigidity of the chelating peptide scaffold, supporting a significant impact of metal-binding on fluorinated peptides. Of note, the potential of fluorinated amino acids as hydrogen-bond donors or acceptors and their influence on microsolvation in biocatalytic metal centres is of high interest. The above insight indicates that these aspects can be studied independently from other effects of fluorination. Initial insights based on vibrational spectroscopy and DFT calculations, using both implicit and explicit solvation models, will be provided.

Search for Novel Superconductors in a Chemical Capacitor Setup

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The discovery of high-temperature superconductors (HTS) in 1986 initiated an enduring pursuit of novel superconducting materials, a research avenue that continues to attract scientists to this day. To achieve superconductivity, parent insulating compounds must be doped with a suitable amount of either electrons or holes. However, many compounds resist any doping attempts. To bypass these difficulties, a "chemical capacitor"[1][2] was designed to simultaneously control charge distribution and induce metallization in diverse compounds[3]. This method leverages the interaction between carefully selected oxidizing and reducing nanolayers, with a separator that modulates the interaction strength by varying its thickness and dielectric constant. In our study, we investigated fluorine compounds as wide gap insulators in the chemical capacitor setup, specifically CaF_2, $CsPbF_3$, KF and $KMgF_3$. Their selection was based on structural compatibility, lattice parameters and electronic band alignment in the following systems: CaF_2 | Si/NaCl | CaF_2, $CsPbF_3$ | LiCl | $CsPbF_3$, KF | NaCl/LiCl | KF and $KMgF_3$ | NaCl/LiCl | $KMgF_3$. Our analysis of these systems was conducted using quantum-mechanical calculations within density functional theory (DFT), employing Quantum ESPRESSO (QE)[4] software suite. It was observed that the layer of atoms in the direct vicinity of the metallized compound played a crucial role in stabilizing the structure. For CaF_2, the lowest free energy was reached when fluorine atoms were close to the metallized nanolayer, whereas in the case of $KMgF_3$, the structure with NaCl between KF layers reached a lower energy than the analogous structure with NaCl between MgF_2 layers. Among the systems of interest, $KMgF_3$ | NaCl | $KMgF_3$ reached the highest stability with a band gap of 5.2 eV. This stability allowed us to dope this system, demonstrating high achievable doping levels of up to 0.3 e^- doping and 0.1 h^+ doping per atom. In the hole doping scenario, it was possible to achieve charge transfer to F^- (2p) orbitals with high density of states along with Cl^- (3p) orbitals. This phenomenon for fluorine is rarely achievable since fluorine serves mainly as an electron-withdrawing agent[5][6] and, in more stable structures, may lead to higher critical temperatures, which in this case was T_c = 68 mK. Electron doping primarily affected high-energy cationic K^+ (3d) and (4s), Mg^{2+} (3s) and Na^+ (3s) states, with a minor contribution from F^- orbitals. Better stability and higher doping level in this case resulted in a higher predicted critical temperature of 0.22 K at 0.2 e^- doping. In conclusion, for both e^- and h^+ doping, we successfully metallized NaCl using $KMgF_3$ as a wide band insulator. In the case of hole doping, F^- (2p) states were the main contributors to the electronic density of states.

References

[1] W. Grochala, *Wiadom. Chem. (Polish)*, **2021,** 75, 755.
[2] D. Jezierski et al., *PHYS CHEM CHEM PHYS,* **2022**, 24, 15705.
[3] A. Grzelak et al., *Angew. Chem. Int. Ed. Engl.*, **2021**, 60, 13892.
[4] P Giannozzi et al., *J. Phys.: Condens. Matter*, **2017**, 29, 465901.
[5] A. James, D. Murphy, S. Zahurak, *Nature*, **1989**, 338, 240.
[6] A. Bortolozo et al., *Mat. Sci. App.*, **2012**, 3, 623.

Regio- and Stereochemical Behaviour of Cyclooctane Derivatives containing CF_2 Moieties

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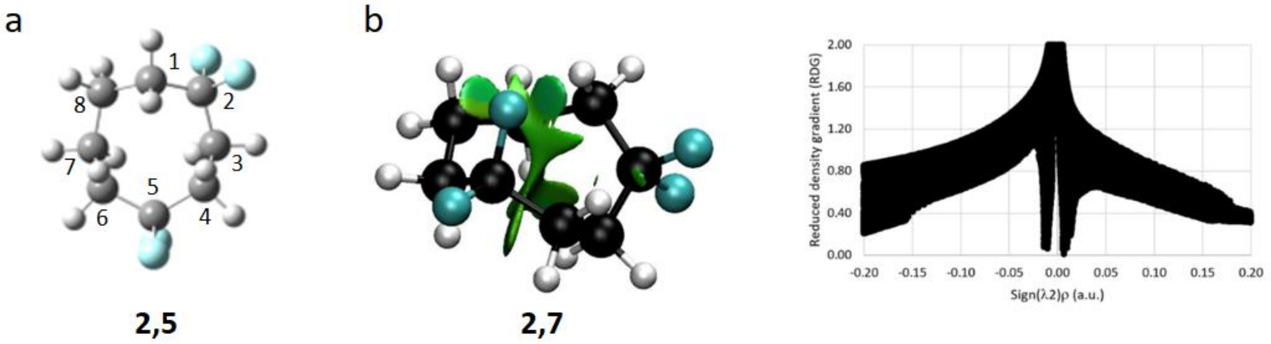
Cyclooctane is a significant medium-sized ring in organic chemistry, with fluorination offering modulation of properties such as conformational energies, polarity, viscosity, and p*K*a. In this quantum-chemical study (B3LYP-GD3BJ/6-311++G**), two CF_2 groups replaced methylene units in the most stable conformation of cyclooctane (boat-chair) [1] to investigate the effects of head, corner, and edge substitution on the energetics of various constitutional and stereoisomeric structures. A comparable study on a square-like cyclododecane derivative revealed that CF_2 groups prefer corner positions to avoid transannular interactions [2]. Sixteen structures with CF_2 groups positioned at 1,2; 1,3; 1,4; and 1,5 relative positions were evaluated. The results indicate that CF_2 groups favor head (C5) and corner (**2,5**, Figure 1a) positions within the cyclooctane ring over head (C1) and edge positions. The latter structures orient fluorines *endo*, leading to transannular repulsion. Notably, the **2,7** isomer, containing an edge CF_2 group, exhibits remarkable stability due to an unprecedented transannular hydrogen bond between the hydrogen at C3 and the CF_2 group at C7 (Figure 1b). This interaction is evidenced by a calculated $^{TS}J_{HF}$ spin-spin coupling constant of 5.0 Hz. When conformationally weighted by the Boltzmann population of the **2,7** isomer, the observable $^{TS}J_{HF}$ coupling constant would be approximately 0.5 Hz.



2,5

2,7

Figure 1. (a) The most stable boat-chair cyclooctane derivative (**2,5**), featuring two CF_2 groups positioned at the corner (C2) and head (C5) positions. (b) NCI surface and RDG plot for the **2,7** structure, illustrating the attractive transannular interaction between the *endo*-oriented fluorine and hydrogen atoms.

References

[1] Pakes, P. W.; Rounds, T. C.; Strauss, H. L. *J. Phys. Chem.*, **1981**, *85*(17), 2469-2475.
[2] Skibinski, M.; Wang, Y.; Slawin, A. M. Z.; Lebl, T.; Kirsch, P.; O´Hagan, D. *Angew. Chem., Int. Ed.*, **2011**, *50*(45), 10581-10584.

Contaminants of Emerging Concern (CECs)

Perfluorinated (PFAS) Pollutants – Molecular Modelling and Simulation for Environmental Remediation

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The extraordinary stability of PFAS and the typically low concentrations at which they are present in the environment generally preclude the use of in-situ methods for their chemical transformation into harmless compounds. Hence, field-implemented remediation processes are generally based on a physical separation method to reduce PFAS concentration in the environmental matrix, while generating a concentrated stream that may be treated subsequently. Adsorption on solids, membrane processes, flocculation, and foam fractionation, are some of the available processes. Knowing the thermophysical behaviour of PFAS is crucial for the design and optimization of all these technologies. Nevertheless, large gaps and inconsistencies exist in the available experimental data, and development must rely frequently on trial-and-error.

In this project, a modelling and simulation approach is used to gain an understanding of the behaviour of PFAS at the molecular level. Molecular models and simulation methods are tested, validated against the available literature results, and then used to obtain properties for related compounds, extrapolate beyond the experimentally studied conditions, or to provide reliable estimates of thermophysical data whenever experimental values are unavailable, disperse or inconsistent. Examples are presented for diffusion coefficients [1] and surfactant properties of carboxylate and sulfonate PFAS in water, including the calculation of adsorption isotherms and structural analysis of the Gibbs films formed.

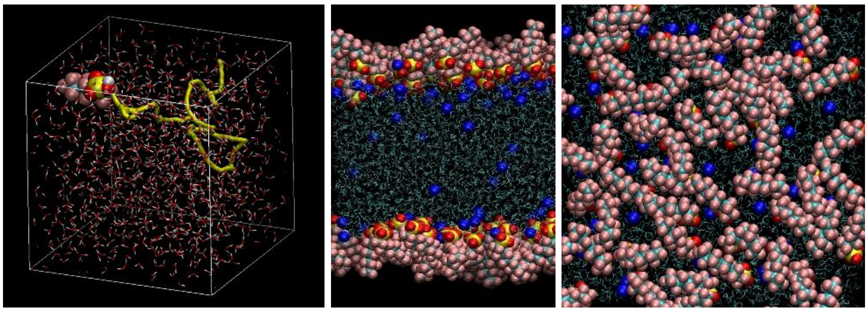

Figure 1. Left to right: Diffusion of perfluorohexanesulfonic acid in water; side- and top-views of a film of NaPFOS adsorbed at the surface of water.

References

[1] Damião, G.; Morgado, P.;* Silva, P.; Martins, L.F.G.; McCabe, C.; Filipe, E.J.M.* *Fluid Phase Equilib.,* **2023**, *575*, 113928.

Adsorption of PFOA and PFOS Using Modified Alumina

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Per- and polyfluorinated substances (PFAS) are persistent organic pollutants of great concern for the environment and human health. The removal of these compounds from water is of great importance. But conventional technologies exhibit limitations in this field. Challenges faced by current removal methods like activated carbon or advanced oxidation processes are for example high energy consumption, low adsorption of short-chain PFAS and regeneration problems [1]. Therefore, a new material is needed for the adsorption of PFAS which offers both high selectivity and reusability while maintaining low costs. Modified alumina could address this gap by providing a high surface area, chemical stability, adjustable surface properties and good availability, making it a promising alternative to conventional adsorbents.

In this study, the effectiveness of modified alumina in PFAS removal was investigated. The experiments were conducted as batch tests using pelletized alumina in deionized water to ensure controlled conditions and reproducible results. Alumina was modified with phosphonates of different chain length containing quaternary ammonium ions. The adsorption performance of the different modifications was evaluated for a solution containing 100 µg/l of PFOA and PFOS.

The results demonstrate that the modification of alumina significantly improves the adsorption efficiency, from 28 % up to 72 % removal of PFOA and from 44 % up to 95% removal of PFOS after 1 h. Further investigations showed that the adsorption performance depends on the concentration of PFAS, with decreased efficiency at higher pollutant levels. Lower pH values led to higher adsorption capacities, while high concentrations of co-existing ions like sulphate and chloride reduced the adsorption efficiency. However, one modified alumina material still maintained a stable performance under moderate salt concentrations, showing the potential of these materials.

With further optimizations it might be possible to increase the adsorption efficiency for PFAS, the robustness and the regeneration ability of the material to develop an easy, sustainable and efficient method for the removal of PFAS from water by using switchable ceramic adsorbers.

References

[1] X. L.; Q. L.; X. Z.; T. K. K.; W. H.; Y. C.; M. E. Z.; D. D. G. *Environ. Pollut.,* **2023**, *Volume 321*, 121138.

Hybrid Constructed Wetlands for Runoff Water Treatment: Efficiency in Removing Organic Pollution and Contaminants of Emerging Concern

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The rapid urbanization worldwide has led to a significant increase in stormwater runoff, posing substantial environmental challenges. As urbanization continues to intensify, addressing these challenges through sustainable solutions becomes increasingly important for protecting vulnerable ecosystems [1]. In this context, Sebkha Sijoumi, a critical wetland in Tunis, Tunisia, is increasingly affected by untreated stormwater and sewage overflows, threatening water quality and ecosystem health [2]. This study assesses the potential of a hybrid constructed wetland (CWs) pilot plant, implemented in *Sebkha Sijoumi*, as a nature-based solution for enhancing runoff water treatment and mitigating pollution (Figure 1). While most research on CWs focuses on organic and nutrient pollution, contaminants of emerging concern (CECs) remain underexplored, highlighting the need for further investigation into their removal efficiency. This study evaluated the capacity of the developed hybrid CW to remove CECs, including Bisphenol A (BPA) and pharmaceuticals (Diclofenac (DFC) and Ofloxacin (OFL)), alongside conventional pollutants and heavy metals. Aluminum was the only heavy metal detected at the inlet (0.04–0.48 mg/L) and was fully removed below detection limits. However, the pilot plant exhibited varying performance in CECs removal. While OFL (382 µg/L) was efficiently reduced to below detection limits (<0.1 µg/L), DFC removal was limited, with only a 13.5% reduction (from 155 µg/L to 134 µg/L). BPA (6.2 µg/L) remained largely unaffected by treatment. COD monitoring across treatment stages indicated system stability during summer, with no impact on biological performance when HRT was reduced from 48 h to 18 h (residual COD ~40 mg/L). However, in winter, COD removal efficiency declined from 76% to 51% at 18 h HRT, requiring an increase to 48 h, which restored efficiency to 74%. Ammonium concentrations remained low, with nearly complete removal at the outlet. While constructed wetlands proved effective in removing organic pollution, additional treatment approaches are required to tackle residual CECs and enhance the overall efficiency of water treatment.

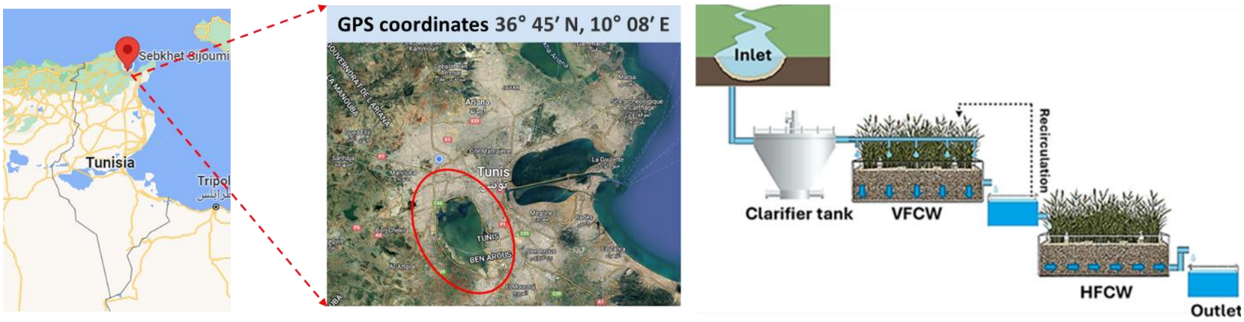

Figure 1. Localisation and layout of the CW pilot plant

References

[1] Kushwaha, A.; Goswami, L.; Kim, B.S.; Lee,. SS.; Pandey, S.K.; Kim, K.H. *Chemosphere*, 2024, 360, 142364.
[2] Guelmami, A.; Chamssidine, C. A.; Labidi, I.; Feltrup-Azafzaf, C., 2023. Technical report. Tour du Valat, Arles (France). 27p.

Development and Characterization of Innovative Materials for Photocatalytic Degradation of Perfluorooctanoic Acid

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Perfluorooctanoic acid (PFOA), a widely used member of per- and polyfluorinated alkyl substances (PFAS) in products like food packaging and non-stick cookware, has been released in the past into the environment in significant amounts and now due to this can be easily found in wastewater. Its stability, due to strong C-F bonds, makes it resistant to degradation [1]. PFOA and other PFAS have been classified as persistent organic pollutants (POPs) due to their harmful effects on human health and the environment [2]. Various methods, including photocatalysis, are being studied to remove PFOA from contaminated water. Photocatalysis shows promise as an effective, eco-friendly solution for PFOA degradation [3].

In this study we developed and characterized different photocatalysts to be used for the degradation of PFAS. We used photocatalysts based on aluminium oxide and zinc oxide, titanium oxide with tungsten oxide and titanium oxide with graphene oxide. The photocatalysts were prepared using the same method, plasma electrolytic oxidation (PEO), which immobilizes photocatalytic compounds on metal substrates such as titanium. This technique, which involves oxidation in an alkaline electrolyte, allows the oxide layer to be easily doped with various components, improving stability and recycling potential. The characterization of the photocatalytic coatings was carried out using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS). To confirm their efficacy, photocatalytic degradation of PFOA in an aqueous solution. Analysis by liquid chromatography and mass spectrometry confirmed that all photocatalysts are effective in PFOA degradation, while titanium oxide with tungsten oxide stood out, removing more than 90% of PFOA within 8 hours, which is expected and in accordance with the structures of the materials that we gained insight into after their detailed characterization.

Acknowledgement

This work was supported by the European Union's Horizon Europe Framework Programme, Twinning Western Balkans, under grant agreement No. 101059534 (PFAStwin).

References

[1] Zango, Z. U., Khoo, K. S., Garba, A., Kadir, H. A., Usman, F., Zango, M.U., Oh, W. D., Lim, J. W., *Environ. Res.,* **2023,** 221, 115326.
[2] Li, K., Gao, P., Xiang, P., Zhang, X., Cui, X., Ma, L.Q, *Environ. Int.,* **2017,** 99 43-54.
[3] Liu, J., Guo, C., Wu, N., Li, C., Qu, R., Wang, Z., Jin, R., Qiao, Y., He, Z., Feng, X., Zhang, Y., Wang, A., Gao, J., *Chem. Eng.*, **2022,** 435, 134627.

Respirometric Analysis for Monitoring the Microbial Activity during Exposure to Perfluorobutanesulfonic and Perfluorohexanesulfonic Acid

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Microbial degradation of per- and polyfluorinated alkyl substances (PFAS) is an emerging area of research for mitigating environmental contamination [1]. While traditional chemical or physical methods struggle to break down these highly stable compounds, certain microorganisms have shown potential in degrading PFAS under specific conditions. These microbes utilize enzymes that can attack the C-F bonds and transform PFAS into less harmful substances. However, the biodegradation process is often slow, and more research is needed to identify efficient microbial strains and optimize environmental conditions [2]. The development of effective bioremediation techniques for PFAS could offer an eco-friendly solution for contamination management [3]. During our study, we conducted an experiment on the transformation of perfluorobutanesulfonic acid (PFBS) and perfluorohexanesulfonic acid (PFHxS) as model substances. In this study, the degradation of PFBS and PFHxS was monitored using a Micro-Oxymax Respirometer (Columbus Instruments, USA). The respirometer is a device that measures the production and consumption of various gases simultaneously. It operates in a 'Closed Loop Measurement Method' mode and measures changes in oxygen consumption and carbon dioxide production during microbial degradation. The microorganisms used were *Pseudomonas* isolated from PFAS-contaminated sites and under a PFAS selection pressure. They were inoculated in three different media: mineral with yeast extract (control), mineral with yeast extract and 5 ppm of PFBS, and mineral with yeast extract and 5 ppm of PFHxS.

Results suggest that all tested strains were active during exposure to PFBS and PFHxS, however one strain of *Pseudomonas* was slightly inhibited by the pollutants, whereas two other tested strains exhibited higher activity in the presence of these compounds compared to the control sample without PFAS. To further analyse the metabolic process involved, concentration of PFBS and PFHxS was monitored, as well as their transformation products.

Acknowledgement

This work was supported by the European Union's Horizon Europe Framework Programme, Twinning Western Balkans, under grant agreement No. 101059534 (PFAStwin).

References

[1] Berhanu, A., Mutanda, I., Taolin, J., Qaria, M. A., Yang, B., Zhu, D., *Sci. Total Environ.*, **2023**, 589, 160010.
[2] Kumar, R., Dada, T. K., Whelan, A., Cannon, P., Sheehan, M., Reeves, L., Antunes, E., *J. Hazard. Mater.*, **2023**, 452, 131212.
[3] Zhang, Z., Sarkar, D., Biswas, J. K., Datta, R., *Bioresour. Technol.*, **2022,** 344, 126223

Fungal Biodegradation of PFAS: Metabolite Formation and Defluorination by *Cunninghamella elegans*

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Per- and polyfluoroalkyl substances (PFAS), including perfluorooctanesulfonic acid (PFOS) and 6:2 fluorotelomer sulfonic acid (6:2 FTSA), are highly persistent environmental contaminants of significant concern due to their bioaccumulation potential and toxicity. This study examines the biodegradation of PFOS and 6:2 FTSA by the fungus *Cunninghamella elegans*, which has previously been shown to degrade perfluorooctanoic acid (PFOA) and fluorotelomer alcohols (FTOHs) [1,2]. Metabolite analysis using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) identified several degradation products, including perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), and 5:3 fluorotelomer carboxylic acid (5:3 FTCA), indicating fungal-mediated transformation. Additionally, fluoride ion release, quantified using a fluoride ion-selective probe and fluorine nuclear magnetic resonance (F NMR), further corroborated PFAS degradation. The detection of these fluorinated metabolites provides new insights into PFAS breakdown pathways and highlights the potential of *C. elegans* for bioremediation applications.

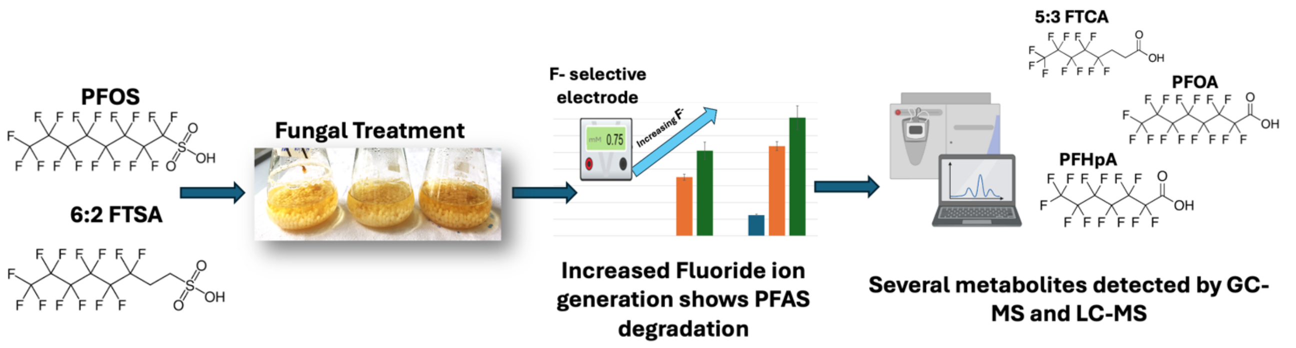

Figure 1. Biodegradation of PFAS by *Cunninghamella elegans*, showing the biotransformation of PFOS and 6:2 FTSA into metabolites including PFHxA, PFHpA, PFOA, and 5:3 FTCA.

References

[1] M.F. Khan; J. Paul Guin; R.K. Thampi; J.A. Sullivan; C.D. Murphy. *Environ. Sci. Pollut. Res*., 30 (**2023**) 91478–91486.
[2] M.F. Khan, C.D. Murphy, Fluorotelomer alcohols are efficiently biotransformed by Cunninghamella elegans, *Environ. Sci. Pollut. Res.*, 30 (**2023**) 23613–23623.

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Enhanced Detection of Fluorinated Nano−Particles in Semiconductor Fabrication via FDTD−Optimized Optical Inspection

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In advanced semiconductor manufacturing, control of fluorinated residues—such as those from photoresists and etching by products—is critical due to their detrimental impact on device yield and reliability. These residues often persist as nano−particles (< 50 nm), which elude detection via conventional optical inspection systems. To address this gap, we developed a comprehensive Finite-Difference Time-Domain (FDTD) simulation framework, incorporating surface termination effects of fluorinated substrates (e.g., $–CF_2$, $–CF_3$ chemistry), multiple ultraviolet–deep−UV wavelengths (266–355 nm), and polarization (S/P modes). This framework precisely models light scattering by fluorinated particles on SiO_2 surfaces. Building on established methodologies that combine FDTD with surface plasmon-enhanced scattering models in nanostructured sensing systems, our simulation identified optimal optical conditions: a 20° incident S-polarized beam at 280 nm yields maximal signal-to-noise ratio for 30 nm CF_2-functionalized silica spheres. We validated these parameters by fabricating fluorinated silica nano−particle samples and performing UV−enhanced dark-field microscopy, achieving a detection threshold down to 28 nm—representing a 40% improvement over traditional inspection limits. Notably, this advancement was realized without additional hardware modifications, enabling in-situ machine vision deployment within existing fab tools. It also facilitates domestic capability for fluorinated contaminant monitoring, reducing reliance on imported proprietary systems. This work opens new pathways for fluorous−material inspection in semiconductor and fluoropolymer−based manufacturing, with implications for both contamination control and materials characterization.

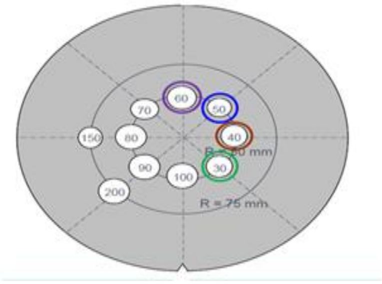

Figure 1. Spatial Distribution of Fluorinated Nano-Particles on a Wafer Surface According to Radial Position.

References

[1] Hasanah, L.; Mutia, R.; Wulandari, C.; Mulyanti, B.; Sahari, S. K. Investigating the effect of surface termination and thickness of MXene on the detection response of the SPR sensor using FDTD simulation. Results in Optics, 2023, 12, 100438.
researchgate.net
[2] Synopsys Glossary. What is Finite-Difference Time-Domain (FDTD) and how does it work

Base-mediated Poly-substitution of Polyfluoroarenes by S_NAr with Terminal Alkynes and Subsequent Fluoride Transfer

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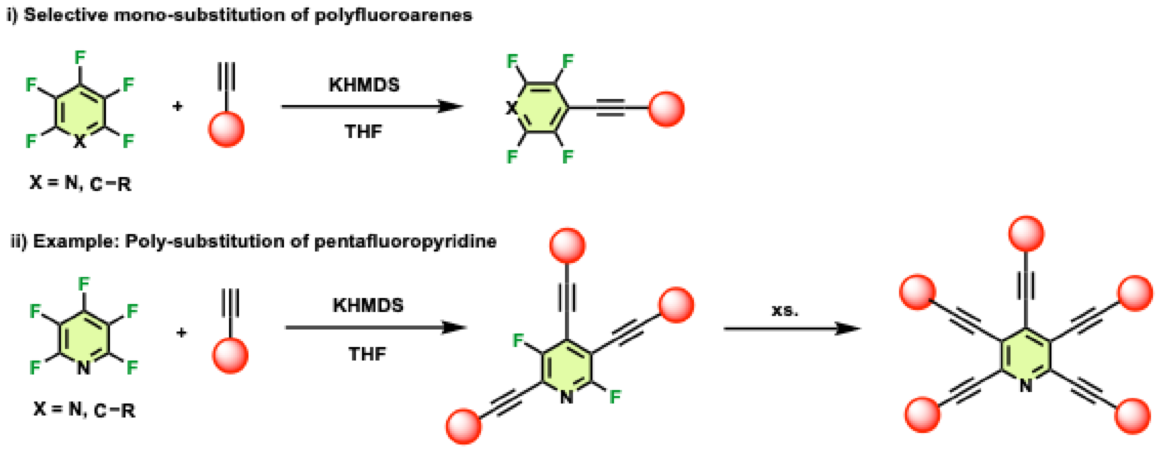
Polyfluoroarene compounds are versatile and cost-effective precursors for the synthesis of valuable defluorinated building blocks through C–F functionalisation. Among these transformations, nucleophilic aromatic substitution (S_NAr) is an attractive route due to its transition metal-free nature, making it highly desirable for applications in pharmaceutical and electronic materials.[1-3] In this study, we present a rapid and efficient S_NAr reaction between polyfluoroarenes and terminal acetylides, mediated by mild bis(trimethylsilyl) amide bases. The resulting substituted alkyne groups exhibit electron-withdrawing effects, enabling further and complete substitutions through stoichiometric adjustments and extended reaction times. Mechanistic insights, supported by extensive DFT calculations, reveal unconventional regioselectivity in the tri-substituted products. These novel compounds were isolated and characterised spectroscopically, highlighting the potential of this methodology for the selective functionalisation of polyfluoroarenes. Furthermore, we present preliminary evidence for a one-pot fluoride transfer to an external electrophile, offering a promising route to improve the atom economy of the overall transformation.



Scheme 1. (i) Monosubstitution of polyfluoroarenes via S_NAr with terminal alkynes; (ii) Sequential polysubstitution of pentafluoropyridine enabled by electron-withdrawing alkynyl groups under mild conditions.

References

[1] C. Liu, H. Zhao, H. Zhao, Z. Wang and B. Zhang, *RSC Adv.*, **2015**, 5, 31993–31997.
[2] M. Shigeno, T. Okawa, M. Imamatsu, K. Nozawa-Kumada and Y. Kondo, *Chem. Eur. J.*, **2019**, 25, 10294–10297.
[3] T. Song, H. Liu, H. Zou, C. Wang, S. Shu, H. Dai, L. Duan, *Angew. Chem. Int. Ed.* **2024**, 63, e202411228.

Effect of HF Treatment Time on Gate–Dielectric Profile Evolution and Cell Speed in 3D Flash Memory

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In the fabrication process of 3D NAND Flash memory, hydrofluoric acid (HF) treatment is commonly performed after channel hole etching within the mold structure to remove native oxide and etch by-products remaining on the sidewalls and bottom of the etched hole. During this step, the inherent etch selectivity of HF between silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) results in differential material removal, as SiO_2 is etched significantly faster than Si_3N_4. This leads to a morphological change in the dielectric profile, wherein the nitride-filled gate region appears relatively more protruded compared to the surrounding oxide spacer, enabling profile modulation at the gate-to-spacer interface. By systematically varying the HF treatment time, we investigated how this profile evolution influences Flash memory cell characteristics, particularly in terms of programming speed and device reliability. The experimental results demonstrate that extended HF treatment enhances gate protrusion, thereby affecting the electric field distribution and charge injection dynamics during programming. This study highlights the critical role of HF process tuning in dielectric profile control and its downstream impact on Flash cell performance.

References

[1] Longjuan, Tang, et al. "Dependence of wet etch rate on deposition, annealing conditions and etchants for PECVD silicon nitride film." Journal of Semiconductors 30.9 (2009): 096005.

Effect of Fluorine Concentration on Self-Passivating Etch Profiles in Advanced DRAM Contact Formation

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In advanced DRAM fabrication, the contact etching process for accessing Active, Word Line (WL), and Bit Line (BL) regions presents a critical challenge due to topographical variation. Specifically, the WL lies lower than the Active region, making it difficult to form contact to the WL without compromising the Active profile. This study demonstrates that by precisely tuning the fluorine content in the plasma chemistry during contact etch, selective formation of a fluorocarbon-based passivation layer occurs on the exposed silicon surfaces. This passivation effectively protects the Active region from lateral or vertical etch damage while allowing the etch to proceed toward the deeper WL region. Through systematic process optimization and profile analysis, we confirm that this fluorine-mediated self-passivation mechanism improves etch selectivity and preserves Active integrity, thereby enhancing device reliability in high aspect ratio contact structures.

References

[1] H. J. Kim et al., “Effect of CF_4/O_2 Plasma Chemistry on Etch Profile and Fluorocarbon Deposition,” Journal of Vacuum Science & Technology B, 2006.
[2] M. J. Kushner, “Modeling of microelectronics plasma processing,” Journal of Physics D: Applied Physics, 2009.
[3] S. Samukawa et al., “Advanced plasma etching for ULSI technology,” Journal of Physics D: Applied Physics, 2006.

Optimization of Asymmetric Fin Profiles to Mitigate Row Hammer in Scaled DRAM through an Etching Process utilizing CF_4

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Row hammer is a critical reliability issue in scaled DRAM devices, causing unintentional bit flips due to frequent access to adjacent rows. This study investigates the use of asymmetric fin profiles in DRAM cell transistors to reduce electric field coupling and suppress 1row hammer-induced failures. We demonstrate that fin asymmetry effectively redistributes charge, reducing disturbance-induced errors compared to symmetric counterparts by TCAD simulation. In order to realize the proposed asymmetric fin structure, an etching technique is required for its physical implementation. HF_3 is typically employed to etch SiO_2 selectively while minimizing Si etching. However, to intentionally form an asymmetric fin profile, we explored a modified gas chemistry by mixing CF_4, which reduces oxide etching and consequently lowers the DC fin height. The proposed structure does not require additional fabrication steps and maintains area efficiency. By introducing fin asymmetry, the influence of electron capture induced by the pass word-line is reduced, leading to a decrease in 1-row disturb D0 failures. These findings suggest a scalable and manufacturable solution to row hammer in future DRAM nodes. These findings provide a promising path forward for reliable DRAM design under aggressive scaling.

References

[1] Yoongu Kim; *et al.* Flipping Bits in Memory Without Accessing Them: An Experimental Study of DRAM Disturbance Errors. *ISCA 2014*
[2] Yeon-Seok Kim; et al. Mitigation of 1-Row Hammer in BCAT Structures Through Buried Oxide Integration and Investigation of Inter-Cell Disturbances. Electronics, 2024

Shedding Light on Mixed-Gas Solubility and Self-diffusivity of Fluorinated Refrigerant Blends in Ionic Liquids with ^{19}F-NMR

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Fluorinated refrigerant gases are receiving increased attention with the implementation of national and international policies and agreements, particularly hydrofluorocarbons (HFCs), which play a crucial role in the formulation of refrigerant blends widely used in both industrial and societal applications. However, due to their high global warming potential (GWP), there is a growing need to develop advanced separation technologies to recover and reutilize low-GWP HFCs while effectively managing high-GWP HFCs to prevent their release into the atmosphere. One promising approach is the design of extractive distillation processes using ionic liquids (ILs) [1]. To perform a successful process design, a fundamental understanding of the solubility of refrigerant blends in ILs is essential. To date, most solubility studies on HFCs in ILs have focused on pure compounds, largely overlooking refrigerant blends due to the complexity and high costs associated with the required analytical and experimental techniques. To bridge this gap, this work proposes the use of ^{19}F Nuclear Magnetic Resonance (NMR) as a powerful and efficient tool for measuring both the solubility and diffusivity of the R-410A refrigerant blend (69.8/30.2 mol % difluoromethane/pentafluoroethane) in one of the most selective ILs, 1-ethyl-3-methylimidazolium dicyanamide ($[C_2C_1im][DCA]$). Mixed-gas solubility was measured at 303.15 K across a pressure range of 0–4 bar and compared with pure-gas solubility under the same conditions. The results revealed no significant mixing effects, suggesting that vapor-liquid equilibrium models based on pure compounds can be reliably applied for process design for this particular system. This trend was also reflected in the self-diffusivity measurements, which showed an increase in gas diffusivity with rising gas mole fraction, likely due to a reduction in liquid-phase viscosity that enhances mass transport phenomena. Overall, ^{19}F-NMR provided valuable insights into the equilibrium and transport properties of multicomponent systems, contributing to the development of efficient and sustainable separation processes for the recovery and recycling of value-added HFCs in the refrigeration sector [2].

Acknowledgements

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References

[1] M. Viar, S. Asensio-Delgado, F. Pardo, G. Zarca, A. Urtiaga, *Sep. Purif. Technol.*, **2023**, 324, 124610.
[2] M. Viar, F. Pardo, G. Zarca, L. Garrido, A. Urtiaga, *Fluid Phase Equilib.*, **2025**, 593, 11343

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