Section régionale Occitanie-Méditerranée
Société Chimique de France
Le réseau des chimistes

PÔLE CHIMIE
UNIVERSITÉ DE MONTPELLIER

Journée Jeunes
Chercheurs & Chercheuses d'Avenir

Conférenciers :

Pr Ulrich B. Wiesner

(Material Science and Engineering, Cornell University)

Dr Nicolas Clavier

(DR CNRS, Institut de Chimie Séparative de Marcoule)

10 juillet 2024

8h45

Amphi Balard,
Campus CNRS

Journées des Jeunes Chercheuses et Chercheurs d'Avenir 2024

Cette journée ***Jeunes Chercheuses et Chercheurs d'Avenir*** est l'occasion, pour les permanent.e.s ayant récemment rejoint le site montpelliérain au sens large (recrutement ou changement d'affectation) et pour les post-doctorant.e.s, de présenter leurs travaux.

Historiquement initiée par la section régionale de la Société Chimique de France il y a une dizaine d'années, cette action est depuis l'an dernier co-organisée avec le Pôle Chimie de l'Université de Montpellier, de façon à proposer une meilleure visibilité à la communauté.

Cette année, cinq permanent.e.s et huit post-doctorant.e.s viendront faire connaître leur recherche au travers de communications orales dans des domaines très variés, illustrant ainsi la richesse thématique du site. La journée sera rythmée par deux conférences invitées données par Ulrich Wiesner (Cornell University, USA) et Nicolas Clavier (ICSM, Marcoule).

Pour la première fois, un prix s'adressant aux post-doctorant.e.s récompensera la meilleure communication orale.

Nous vous souhaitons une très bonne journée scientifique ainsi que des échanges fructueux lors des pauses café et déjeuner !

Programme

8h30 – 8h45	**Accueil des participants**
8h45 – 9h00	**Ouverture** Armelle Ouali, pour le bureau SCF-OM Joulia Larionova, pour le Pôle Chimie
9h00 – 9h45	***Plenary lecture*** **Pr Ulrich B. Wiesner** *(Material Science and Engineering, Cornell University)* “Ultrasmall fluorescent silica nanoparticles for bio-imaging and therapy applications in oncology”
9h45 – 10h05	**Dr Camille BAKKALI-HASSANI** *(Chargé de recherche CNRS, ICGM)* “La catalyse : du contrôle de polymérisation au contrôle des propriétés des matériaux “
10h05– 10h25	**Dr Cécile ECHALIER** *(Maître de conferences UM, IBMM)* “Silylated peptides: what are they for?”
10h25 – 10h40	**Pause - café**
10h40 – 11h00	**Dr Bruno SENJEAN** *(Chargé de recherché CNRS, ICGM)* “Quantum computing for quantum chemistry using qudits ”
11h00– 11h20	**Dr Marie SIMONNET** (Ingénieur-Chercheur CEA, ICSM) “Solvent extraction: recycling and decontamination”
11h20 – 11h40	**Dr Coline PINESE** (Maître de conferences UM, IBMM) “Conception d'encres photosensibles biodégradables, à base de gélatine-tyramine/PLA-6 bras-tyramine, compatibles avec l'impression 3D par polymérisation deux photons et la régénération du tissu méniscal.”
11h40 – 11h55	**Dr Pierre DELLIÈRE** *(post-doctorant ICGM)* “Side reactions in bio-based thermoset poly(furfuryl alcohol), a source of tunability”
11h55- 12h10	**Dr Amal BOUAMMALI** *(post-doctorante ICGM)* “Synthèse de complexes de lanthanides divalents par activation C–P sélective “
12h10 – 13h30	**Pause déjeuner**
13h30 – 14h15	***Conférence plénière*** **Dr Nicolas CLAVIER** *(ICSM - Univ Montpellier, CEA, CNRS, ENSCM, Marcoule)* “Making the nuclear fuels of the future: new paths for actinide oxide synthesis”
14h15 – 14h30	**Dr Arnaud DE ZORDO-BANLIAT** *(post-doctorant ICGM)* “Oxidation of perfluoroalkylselenides “
14h30– 14h45	**Dr Klaudia KVAKOVA** *(post-doctorante IBMM)* “Visualization of sentinel lymph nodes with mannosylated fluorescent nanodiamonds”
14h45 – 15h00	**Dr Alejandro DIAZ-MARQUEZ** *(post-doctorant ICGM)* “Computational-aided development of MOF mixed matrix membranes“
15h00 – 15h15	**Dr Francesco CALZAFERRI** *(post-doctorant IBMM)* “3-Bromo-3-chloro-2-methoxyflavanone: a novel potent and stable small molecule targeting DNA methyltransferases for cancer treatment”
15h15 – 15h30	**Dr Ashakiran MAIBAM** *(post-doctorant ICGM)* “Nitrogen reduction in two-dimensional materials: DFT and beyond**“**
15h30 – 15h45	**Dr Valentin DIEZ-CABANES** *(post-doctorant ICGM)* “Engineering mof/carbon nitride heterojunctions for effective dual photocatalytic co_2 conversion and oxygen evolution reactions”
16h00	**Remise de prix et clôture de la journée**

CONFERENCES PLENIERES

Ulrich (Uli) Wiesner studied Chemistry at the University of Mainz, Germany, and UC Irvine, CA. He gained his Ph.D. in 1991 in Physical Chemistry with work at the Max-Planck-Institute for Polymer Research (MPI-P), Mainz, on holographic information storage in polymer liquid crystals. After a two-year postdoc at E.S.P.C.I. in Paris, France, on local dynamics-mechanical property correlations in polyesters, he returned to the MPI-P in 1993. In 1998 he finished his Habilitation with work on block copolymers under oscillatory shear and block copolymer ionomers and received tenure as an MPI-P staff member. He joined the Cornell University, NY, Materials Science and Engineering (MSE) faculty in 1999 as a tenured Associate Professor, became a Full Professor in 2005, and since 2008 is the Spencer T. Olin Professor of Engineering. At Cornell, he holds secondary appointments (field membership) in Chemical and Biomolecular Engineering (CBE), Biomedical Engineering (BME), and Chemistry and Chemical Biology (CCB). Since January of 2023 he is an inaugural faculty member of the multi-college Department of Design Tech at Cornell and Professor of Design Tech. Since his arrival at Cornell, he has worked at the interface between polymer science and inorganic/solid-state chemistry with the goal to generate multifunctional nanomaterials for applications including energy conversion and storage, clean water, and nanomedicine. From 2015-2021 he was the co-director of the MSKCC-Cornell Center for Translation of Cancer Nanomedicine (MC^{2}TCN), one of six Centers for Cancer Nanotechnology Excellence (CCNE) funded by the NCI (https://www.cancer.gov/sites/ocnr/research/alliance/ccne).

Selected Honors and Awards

2023: Charles G. Overberger International Prize for Excellence in Polymer Research of the American Chemical Society
2022-2023: Distinguished Israel Pollak Lecturer, Technion, Israel
2022: Fiona Ip Li ’78 and Donald Li ‘75 Excellence in Teaching Award, Cornell University
2021: National Science Foundation Creativity Award
2019: Selected “*Ambassadeur pour la Chimie Française*”, Institute of Chemistry, CNRS, France
2018: College of Eng., Nanyang Technological Univ., Singapore, Distinguished Speaker Award
2016: Arthur K. Doolittle Award of the American Chemical Society PMSE Division
2015: Cornell Engineering Research Excellence Award, Cornell University
2015: Elected PMSE Fellow of the American Chemical Society
2008: National Science Foundation Creativity Award
2005: Mr. & Mrs. Richard F. Tucker’50 Excellence in Teaching Award, Cornell University
2001: IBM Faculty Partnership Award
1999: Carl Duisberg Memorial Award of the German Chemical Society (GDCh)

Technology Commercialization

2016-present: Cofounder Elucida Oncology, Inc.; effort to commercialize C dots for applications in oncology (http://www.elucidaoncology.com); Director, Co-Chair of Scientific Advisory Board.
2013-present: Cofounder TeraPore Technologies, Inc.; effort to commercialize block copolymer based ultrafiltration (UF) membranes (https://teraporetech.com).

ULTRASMALL FLUORESCENT SILICA NANOPARTICLES FOR BIO-IMAGING AND THERAPY APPLICATIONS IN ONCOLOGY

Prof. Ulrich B. Wiesner
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Since the end of the nineties, the promise of the use of particles in nanomedicine has been enthusiastically embraced by the scientific community with significant research activities worldwide. Today, more than twenty years later, a major breakthrough in the use of nanoparticles for diagnostic and, in particular, therapeutic applications in medicine has still not materialized. In the case of applications in oncology, this has to do with a number of issues encountered with delivery approaches of particles in the tens of nanometers range (or larger), including non-favorable particle biodistribution (BD) and pharmacokinetics (PK) with significant accumulation at off-target sites like liver and spleen, low targeting efficiencies, low penetration of solid tumors, as well as difficulties in scaling up synthesis approaches. In this presentation an ultrasmall fluorescent dye-encapsulating silica core – poly(ethylene glycol) shell (core-shell) nanoparticle platform (Cornell dots, or simply C dots) is described with diameters below 10 nm that overcomes a number of these issues. Renally cleared C dots can be surface functionalized with various targeting moieties, including small peptides and antibody fragments, providing high target affinity, as well as large numbers (up to 40) of pharmaceutical drugs, leading to extremely high drug loading capacities. The talk will describe the synthesis, characterization as well as physicochemical and biological properties of these organic-inorganic hybrid particles, including in vitro and in vivo experiments all the way to diagnostic and therapeutic human clinical trials. The work demonstrates that C dot behavior is distinct from most other existing delivery vehicles including antibody-drug conjugates, rendering them exciting and promising candidates for currently ongoing clinical translation.

Nicolas Clavier studied chemistry at the University of Montpellier and earned his PhD in Radiochemistry from the University of Paris-Sud in Orsay in 2004. Following a postdoctoral position at the military division of CEA, he became a CNRS researcher in 2006. Currently, he serves as CNRS Research Director at the Marcoule Institute for Separation Chemistry (ICSM, UMR 5257 Univ Montpellier, CEA, CNRS, ENSCM).

Nicolas Clavier has extensive experience in the synthesis, sintering, and characterization of ceramic materials relevant to the nuclear fuel cycle. His work includes the development of uranium and thorium-based SIMFuels, phosphate-based wasteforms for actinide conditioning in underground repositories, and synthetic analogues of uranium-bearing minerals. He specializes in innovative synthesis methods, particularly using hydrothermal conditions, and investigates the relationships between the ceramics' fabrication process, final microstructure, and properties such as chemical durability, ionic conductivity, and radiation damage resistance.

He has participated in several European H2020 Euratom projects and international collaborations and has worked on applied research with industrial partners. He has published over 120 peer-reviewed research papers, and supervised 13 PhD students, and 28 MS students. In 2012, he was awarded the CNRS Bronze Medal.

MAKING THE NUCLEAR FUELS OF THE FUTURE: NEW PATHS FOR ACTINIDE OXIDE SYNTHESIS

N. Clavier, S. Benarib, J. Manaud, J. Martinez, V. Trillaud, R. Podor, J. Maynadié, N. Dacheux

ICSM - Univ Montpellier, CEA, CNRS, ENSCM, Marcoule

Powder metallurgy processes are commonly used for the preparation of mixed actinide and/or lanthanide oxides, e.g. in the fabrication of the MOx nuclear fuel (Mixed Oxide: $(U,Pu)O_2$) used in some of France's nuclear reactors. However, future developments, such as the use of other technologies (fast-neutron reactors) and the multi-recycling of plutonium, call for a rethinking of these processes, in particular to produce more homogeneous compounds with optimized physico-chemical properties. With this aim, wet chemistry routes, based on the precipitation of low-temperature precursors (oxalates, carbonates, etc.) and their subsequent conversion to oxide during high-temperature heat treatments, have been envisaged for years. However, the latter can be accompanied by a number of drawbacks, such as the presence of residual carbon in the samples, or morphologies unfavourable to sintering.

In this context, the ICSM's Evolving Interfaces in Materials group has been working for several years on the development of original synthesis routes enabling direct transition from cations in solution to oxides, notably through the use of "mild" hydrothermal conditions (typically $200 < T < 250°C$, $t = 5 - 24$ h). These lead to decomposition of the organic ligands initially used in the precipitation step, followed by hydrolysis of the cations. By way of example, recent work on the hydrothermal conversion of uranium(IV) oxalate has shown that adjusting the experimental conditions (temperature and duration of hydrothermal treatment, pH of the reaction medium) effectively eliminates residual carbon (up to levels of the order of 100 ppm) and shapes the morphology of the resulting powders. At the same time, in-situ X-ray absorption spectroscopy studies at the uranium L_3 edge have helped to clarify the chemical mechanisms behind this conversion.

This presentation will focus on several original synthesis routes leading to actinide and/or lanthanide oxides with controlled morphologies, typically ranging from nanopowders to spherical microparticles. The impact of morphological and chemical modifications induced by the synthesis routes will then be illustrated through different oxide powder properties and potential applications.

PRESENTATIONS DE JEUNES CHERCHEUSES ET CHERCHEURS D’AVENIR

LA CATALYSE : DU CONTROLE DE POLYMERISATION AU CONTROLE DES PROPRIETES DES MATERIAUX

Camille Bakkali-Hassani[1]

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Année de recrutement : 2023

Keywords: Controlled Polymerisation, Catalysis, Vitrimers, Rheology.

Summary:

La plupart des avancées majeures de la chimie des polymères découle des évolutions techniques et synthétiques de la chimie organique.[1] La catalyse, pilier de la chimie verte, a révolutionné notre approche de la synthèse organique, du contrôle des polymérisations mais aussi du contrôle des propriétés rhéologiques et thermo-mécaniques des matériaux polymères. Cette présentation centrée sur l'apport de la catalyse dans la chimie des polymères résumera les expériences qui ont jalonné mon parcours de jeunes chercheurs jusqu'à mes travaux actuels au sein de l'Institut Charles Gerhardt. Ces travaux se sont principalement concentrés sur la catalyse au service de la chimie des polymères à travers différents axes comme (i) le contrôle et la sélectivité de transformation chimique (ii) le contrôle de polymérisation[2] (iii) le contrôle des propriétés vitrimères ou rhéologiques des matériaux[3] (Figure 1).

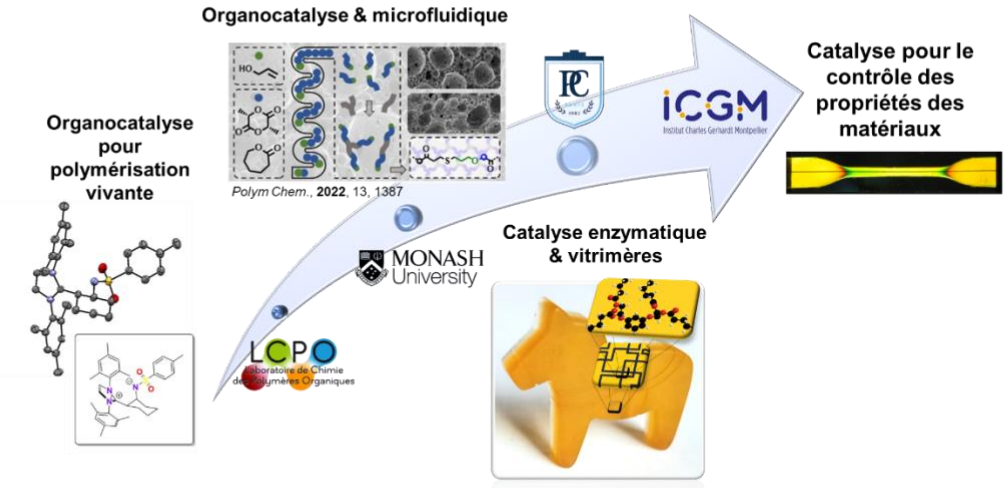

Figure 1. La plupart des avancées majeures de la chimie des polymères

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SILYLATED PEPTIDES: WHAT ARE THEY FOR?

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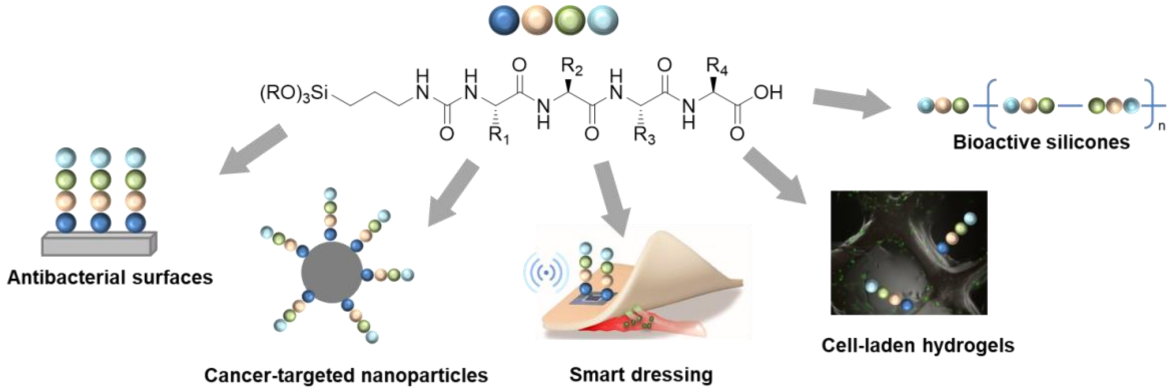
Année de recrutement : 2023

Keywords: sol-gel; biomaterials; biorthogonal chemistry; hybrid peptides; bioactive sequences

Summary: The introduction of alkoxysilane groups onto peptides yields silylated peptides that can be used as precursors to prepare tailor-made materials via the sol-gel process. Compatible with fragile biomolecules, the sol-gel chemistry proceeds under mild conditions to create covalent siloxane bonds between different silylated building blocks or silanol-presenting surfaces.[1] This can be used to synthesize and/or functionalize materials. We reported grafting of silylated peptides onto silicone catheters to fight against bacterial colonization[2] and onto an electrical sensor to monitor chronic wounds. Interestingly, different silylated peptides can be combined to yield multi-ligand nanoparticles with an accurate control over the grafting ratio.[3] Beyond grafting, silylated peptides can also be used alone or in combination with other silylated precursors for the direct synthesis of functional polymers[4] and hydrogels.[5] Live cells, in particular stem cells, can be encapsulated in hydrogels without affecting their viability and function.[6] Cell-laden solutions can be used as bioinks to 3D print scaffolds for tissue engineering.[7]
Given the wide range of biological activities associated with peptide sequences, the use of silylated peptides provides highly interesting properties to the resulting materials, highlighting the potential of the sol-gel chemistry for the design of tailor-made biomaterials.



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QUANTUM COMPUTING FOR QUANTUM CHEMISTRY USING QUDITS

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Année de recrutement : **2020**

Keywords: Electronic structure theory, quantum computing, qudits, wavefunction theory, density functional theory, quantum algorithms

Summary: Quantum computers have shown promises to solve problems that are currently intractable on classical computers [1]. While quantum chemistry has been identified as one of the killer applications of quantum computers in the near term, the focus is on wavefunction theory that provides an exact solution of the quantum problem [2-4]. However, the focus on these specific cases turns out to be extremely limited in term of size of affordable system (even on quantum computers). Currently, quantum algorithms are almost all qubit-based, meaning that their quantum units are two-level systems, i.e. a superposition of states 0 and 1. In this talk, we will generalize such algorithms to qudit-based machines, where a qudit is a d-level system which state can be a superposition of d states rather than 2 only. Such a generalization is expected to reduce the circuit depth of the circuits, thus speeding-up the transition toward a possible quantum advantage for chemistry. In a near future, we plan to experimentally realize these algorithms on a new quantum platform based on qudits [5].

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Solvent Extraction : Recycling and Decontamination

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Position actuelle : Ingénieur-Chercheur au CEA Marcoule (ICSM)

Année de recrutement : 2023

Keywords: Solvent extraction; Critical metals; Spent nuclear fuel

Summary:

Solvent extraction is one of the most used separation technics to selectively recover one or several elements from a mixture. It consists in contacting two immiscible phases to perform the transfer of the targeted elements from one phase to the other. Despite using this method for decades, extraction mechanisms are still controversial and further fundamental studies are required to master all parameters. A better understanding can yield new solutions to some important applications such as the recovery of critical materials from urban waste (recycling) or the extraction of heavy metals and/or radioactive elements for decontamination purposes.

During this presentation, the focus will be on the overlooked counterion effect with two examples, the separation of adjacent lanthanides by phenanthroline carboxamides aiming at improving the current separation processes of rare earths (critical materials) and the recovery of radioactive Cs from contaminated saline brines. Indeed, neutral extractants used in my studies extract the target cations with one or several anions to keep the charge neutral. The nature of this anion was found to impact not only the efficiency of the extraction but also the selectivity. In addition, some anions impact the extraction differently depending on the diluent, bringing even more puzzling results.

Several proposals on the topic (ANR, NEEDS) were thus submitted last year to pursue the investigation of this intriguing effect, with the hope that we could propose a more complete model of solvent extraction able to predict these abnormal effects.

Conception d'encres photosensibles biodégradables, à base de gélatine-tyramine/PLA-6 bras-tyramine, compatibles avec l'impression 3D par polymérisation deux photons et la régénération du tissu méniscal.

Coline PINESE[1]

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Position actuelle : Maître de conférences UM

SIDE REACTIONS IN BIO-BASED THERMOSET POLY(FURFURYL ALCOHOL), A SOURCE OF TUNABILITY

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Position actuelle : Post-doctorant

Année de recrutement : Décembre 2023

Keywords: Bio-based thermoset; Poly(furfuryl alcohol); Side-reactions

Summary:

Poly(furfuryl alcohol) (PFA) is among the earliest commercially available bio-based polymers. PFA is a thermoset with excellent chemical and thermal resistance although is can be quite brittle.[1] [1] Nowadays, it is mostly employed in the foundry industry to manufacture metal casting molds. The properties of PFA emerge from its tight network of furfuryl moieties linked by Diels-Alder adducts.

In this communication, a new way to apprehend the PFA will be presented through the use of furan ring opening side-reactions. The carbonyls entities resulting from the ring opening were quantified using quantitative ^{19}F NMR and potentiometry. Procedures to tune the carbonyl content of PFA were assessed. The addition of water at the beginning polymerization was highlighted as the dominant factor. Furthermore, a deep investigation involving structural elucidation technics was conducted to better understand the chemical environment of carbonyls within PFA. It was shown that the furans in PFA are susceptible to both hydrolytic and oxidative ring-opening (Figure 1). When the furan ring opens through the oxidative pathway, the resulting products are conjugated 1,4-ketoaldehydes, which inherently are prone to undergo Diels-Alder reactions, thereby inducing surface crosslinking.[2,3] [2,3] On the basis of this accumulated knowledge, the carbonyl groups in PFA were functionalized with flexible primary amines.[4] [4] This presentation will highlight key results obtained during the development of new tunable PFA materials.

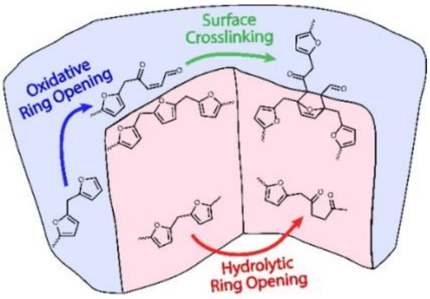

***Figure 1**: Ring-opening reaction occurring in and on PFA resins*

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Synthèse de complexes de lanthanides divalents par activation C–P sélective

Amal Bouammali[1], Asma Allagui,[1,2] Soufiane Tioul,[2] Angus Shephard,[3] Peter Junk,[3] Florian Jaroschik[1]

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Année de recrutement : 2023

Keywords: Lanthanides divalents; Polyarylcyclopentadiényle; Activation C-P ; Complexes sandwich

Summary: Les complexes sandwichs divalents volumineux de lanthanides suscitent actuellement un grand intérêt dans le domaine de la recherche scientifique eu égard à leur stabilité, leur réactivité et leurs propriétés physiques incontournables.[1] Les ligands à base de polyarylcyclopentadiényle semblent des candidats très prometteurs dans la synthèse de ce type de structures, en raison de leurs propriétés stériques et électroniques stabilisantes.[2] D'autre part, des substituants sur les aryles peuvent être facilement introduits lors de la synthèse du ligand, ce qui permet d'améliorer la solubilité des complexes et d'influencer ses paramètres électroniques. Récemment, nous avons rapporté une voie de simple de formation des complexes de lanthanide divalents (Sm, Eu, Yb) à partir du pentaphenylcyclopentadiène portant un groupement partant (GP) de type PPh_2 par clivage sélectif de la liaison C(Cp)–P.[3] Afin d'explorer les potentialités de cette méthode, nous nous sommes intéressés à étendre son champ d'application à l'utilisation d'autres pro-ligands, en particulier $C_5Ph_5P(O)Ph_2$ et $C_5Ph_5P(S)Ph_2$. Nous allons également présenter des aspects mécanistiques de ces transformations.

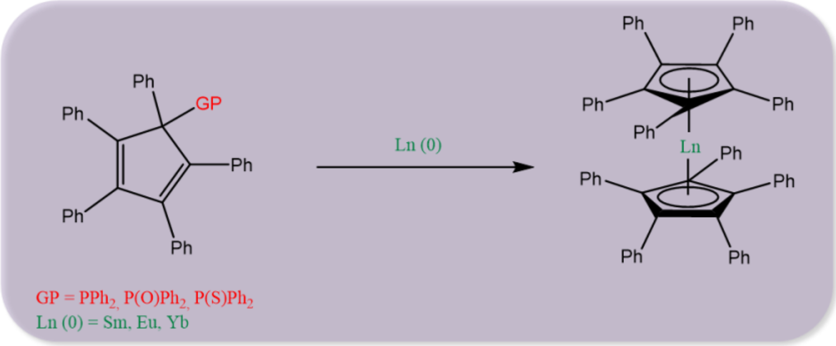

Schéma 1 : Synthèse des complexes sandwichs divalents par activation C-P sélective

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Oxidation of perfluoroalkylselenides

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Arnaud De Zordo-Banliat,[1] Guillaume Dagousset,[1] Bruce Pégot,[1] Emmanuel Magnier[1]

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Année de recrutement : 2023

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Keywords: Selenium, fluorine, oxidation, lipophilicity

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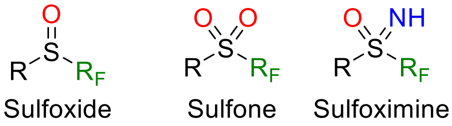
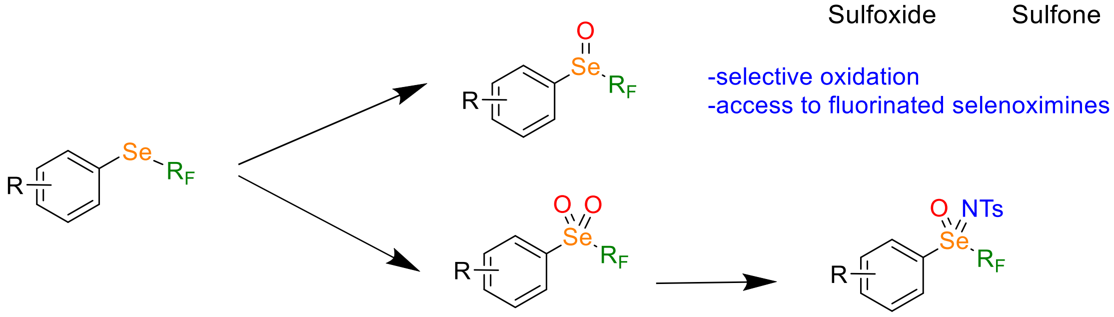
Summary:

For several years, the emergence and the development of fluorinated groups have taken a prominent place in the scientific community.[1] More recently, there has been a growing interest in the synthesis of groups combining fluorine and selenium, in particular because of the high Hansch-Leo lipophilicity parameter (Π_{SeCF_3} = 1.61) which contributes to improve the bioavailability of molecules.[2] Surprisingly, if the S-perfluoroalkylsulfoxides, sulfones, and even sulfoximines are widely known, the oxidation of $SeCF_3$ (or more generally SeR_F) motif has barely been studied. Indeed, although selenoxides and selenones are widely represented in the literature, perfluorinated versions of these molecules have been scarcely described[33] and fluorinated selenoximines have not yet been reported.[4]





The continuity of our work in the laboratory on the trifluoromethylselenolation[5] reaction has led us to develop new approaches in order to selectively obtain perfluoroalkylated selenoxides and selenones. Finally, the first formation of perfluorinated selenoximines will be presented as well as the study of their lipophilicity.

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VISUALIZATION OF SENTINEL LYMPH NODES WITH MANNOSYLATED FLUORESCENT NANODIAMONDS

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Keywords: nanodiamond, polyglycerol coating, mannose targeting, sentinel lymph node visualization

Summary:

Our study focuses on developing an innovative imaging strategy for sentinel lymph node (SLN) visualization employing high-performance near-infrared emitting fluorescent nanoprobes – fluorescent nanodiamonds (FNDs). The FNDs show unique optical properties, such as unlimited photostability and almost quantitative quantum yield. Moreover, FNDs are non-toxic, biocompatible, and modifiable materials. The properties mentioned above make FNDs suitable candidates for bioimaging applications.

First, ultrabright 200 nm-sized fluorescent nanodiamonds were precisely separated by fractional centrifugation. Afterward, FNDs were coated by an alkyne-functionalized polyglycerol layer, which enhanced the biocompatibility of the FNDs and enabled surface modifications via bioconjugation techniques. The polymer coated FNDs were further functionalized by Dmannose using CuAAC click, resulting in exceptionally colloidally stable nanoparticles. *In vitro* experiments showed a significant increase in the internalization of mannosylated FNDs into mouse macrophages (J774A.1) compared to non-mannosylated FNDs. The internalization occurred specifically via the mannose receptor (CD206), which was evidenced by blocking the receptor using another CD206 ligand (mannan) as well as an anti-CD206 antibody (15.2 mAb). *In vivo* experiments confirmed increased retention of mannosylated FNDs in mouse sentinel lymph nodes. Based on these results, mannosylated FNDs could have potential in sentinel lymph node visualization as an intraoperative imaging tool for robotic image-guided surgery.[1]

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COMPUTATIONAL-AIDED DEVELOPMENT OF MOF MIXED MATRIX MEMBRANES

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Année de recrutement : 2022

Keywords: Molecular simulations; Metal organic frameworks; Mixed matrix membranes; MOF/polymer interfaces; Gas separation.

Summary: Mixed matrix membranes (MMMs) incorporating Metal-organic frameworks (MOFs) into polymeric matrices show promising properties for several industrial applications, such as gas separation, water desalination and pervaporation. MMMs have attracted a great attention due to their potential for merging the processability of polymers and the excellent selectivity of MOF materials. Therefore, understanding/prediction of the MOF/polymer interface and gas transport throughout the whole MMMs is of significant importance.[1] In this context, we have recently developed a fully automated computational procedure for generating a library of MMMs and analysing their interfacial structuring based on graph theory. We initiated the process by selecting a series of representative channel-like MOFs (KAUST-8, KAUST-7-Mixed Linkers, CALF20, MIL-53-NH_2, and Zr-fcu-fum) as fillers and a series of polymers with distinct chemical, structural, and mechanical features and we automated our previously established quantum/force field computational method to generate the corresponding composites.

As a representative MMM system, the in-silico created AlFFIVE-1-Ni (KAUST-8) MOF/Polymer of Intrinsic Microporosity-1 (PIM-1) composite was predicted to exhibit a vestibular-pore shape nano-structuring at the MOF/polymer interface. These simulations revealed that the interfacial pore geometry of AlFFIVE-1-Ni/PIM-1 provides optimal guidance of gas molecules and minimizes the molecular entrance effects into the ultra-small channels of the MOF, crucially leading to an acceleration of molecular transport all along the MMM. Subsequent Grand Canonical Monte Carlo and concentration gradient-driven molecular dynamics (CGD-MD) simulations were further performed to assess the thermodynamic and dynamic adsorption CO2 properties of these MMMs. This computational prediction directed the fabrication of the [001] oriented nanosheet AlFFIVE-1-Ni/PIM-1 MMM that was demonstrated to exhibit an excellent CO2 permeability while retaining very good CO_2/CH_4 selectivity.

As a further step, our automated computational procedure identified a variety of distinct interfacial shapes in AlFIVE-1-Ni/polymer systems, along with different degrees of polymer penetration depending on the pore size/shape of the 1D-channel MOFs. The next step involves leveraging these advances by training a machine learning algorithm to enhance the effectiveness of our force field-based Molecular Dynamics analysis of the MOF/polymer interface. This approach will enable us to analyse large MOF/polymer interface datasets more efficiently and accurately, accelerating our progress towards developing optimal MMMs for gas separation.

Acknowledgements

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3-BROMO-3-CHLORO-2-METHOXYFLAVANONE: A NOVEL POTENT AND STABLE SMALL MOLECULE TARGETING DNA METHYLTRANSFERASES FOR CANCER TREATMENT

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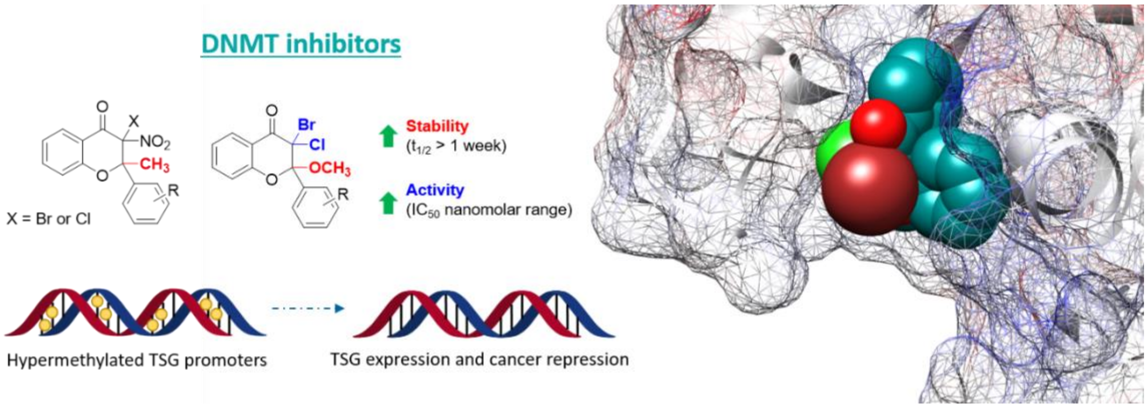
Keywords: DNMT inhibitors, flavanones, epigenetics, DNA methylation, cancer treatment

Summary: DNA methylation, catalysed by DNA methyltransferases (DNMTs), is an epigenetic modification that regulates gene expression. In cancer, the methylation pattern of several tumour suppressor genes (TSGs) is altered, leading to their silencing, and contributing to cell proliferation and tumour progression. Non-nucleoside DNMT inhibitors (DNMTi) were developed to replace the use of nucleoside DNMTi in the clinic, which show low chemical stability and toxic side effects.[1] Our group previously discovered 3-halo-3-nitroflavanones as non-nucleoside DNMTi and optimised their activity in vitro.[2-3] As part of the optimisation process, we recently improved compound stability by inserting a methyl and methoxide substituent at position 2 of the flavanone scaffold. Moreover, we increased compound activity by replacing the nitro group with an additional halogen at position 3. Compounds chemical stability was assessed by HPLC and their inhibitory activity evaluated on purified DNMT enzymes. The most active compound, *anti*-3-bromo-3-chloro-2-methoxyflavanone was able to induce *p15* and *p16* TSG re-expression in HCT-116 colorectal cancer cells. To the best of our knowledge this compound represents the most potent non-nucleoside compound targeting DNMTs, thus representing a valuable molecule for further development in epigenetic reprogramming-based anticancer therapy and chemical biological applications.



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NITROGEN REDUCTION IN TWO-DIMENSIONAL MATERIALS: DFT AND BEYOND

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Année de recrutement : 2024

Keywords: Nitrogen reduction reaction; Density Functional Theory; Limiting potential; Electrocatalyst

Summary:

Sustainable large scale ammonia production from N_2 under mild conditions has been explored through catalyst design with computational tools. Two-dimensional (2D) materials can be exploited as electron reservoirs and its electrons can be tapped and directed to the anti-bonding orbital of N_2 through metallic or non-metallic single atom catalyst (SAC) or catalytic centres introduced as surface modifications. Density Functional Theory (DFT) study implemented with N-N bond activation and N_2 chemisorption as two crucial factors[1] showed metal SAC anchored graphene to be a recyclable heterocatalyst capable of ammonia fixation under mild temperature and pressure with an energy barrier of 1.2 eV.[2] Al-clusters anchored on divalent-vacancy graphene showed a reduction in the energy barrier to 0.78 eV.[3] Another environment friendly approach to ammonia fixation is the electrocatalytic nitrogen reduction reaction (eNRR), and catalytic efficiency of two electrically conductive 2D materials–Mo_2C and vanadium dichalcogenides (VX_2) are further studied and the conductive nature of these 2D substrates enhances the process of electron transfer from the catalyst. Non-metal atomic center, boron when introduced as adatom on defective Mo_2C improves NRR performance to 0.57 eV[4] and the same non-metallic boron atom center when introduced as a substitutional dopant on 2H-phase of VS_2 shows a further reduction in NRR performance to 0.22 eV.[5] Moving forward with the goal of obtaining commercially viable catalysts that do not involve tedious and sophisticated synthesis protocols that are mandatory for the above-mentioned materials, we have studied porous coordination compounds that can be achieved via reticular synthesis. Two-dimensional metal organic framework (MOF) comprised of porphyrin ligands and early transition metals are investigated for ammonia production at ambient aqueous condition, and Ti-based porphyrin MOF is being proposed as an active electrocatalyst for NRR with limiting energy barrier of 0.35 eV in aqueous solvent.[6] The research highlights the aspect of implementing earth abundant metals and non-metals on several 2D materials to develop an active, low cost, stable and efficient electrocatalyst for NRR via an exhaustive DFT study. Moving beyond ab-initio investigation, Grand Canonical Ensemble (GCE) method with DFT and machine learning models will give a comprehensive NRR mechanism inclusive of thermodynamic, kinetic and electrochemical factors that will encompass experimental conditions.

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ENGINEERING MOF/CARBON NITRIDE HETEROJUNCTIONS FOR EFFECTIVE DUAL PHOTOCATALYTIC CO_2 CONVERSION AND OXYGEN EVOLUTION REACTIONS

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Année de recrutement: 2022

Keywords: Photocatalysis, Hybrid Porous Materials, Heterojunctions, Interfacial Charge Transfer.

Summary: Photocatalysis appears as one of the most promising avenues to shift towards sustainable sources of energy, owing to its ability to transform solar light into chemical energy, e.g. production of chemical fuels via oxygen evolution (OER) and CO_2 reduction (CO_2RR) reactions. Ti metal-organic frameworks (MOFs) and graphitic carbon nitride derivatives, i.e. poly-heptazine imides (PHI) are appealing CO_2RR and OER photo-catalysts respectively. Engineering of an innovative Z-scheme heterojunction by assembling Ti-MOFs and PHI offers an unparalleled opportunity to mimic an artificial photosynthesis device for dual CO_2RR/OER catalysis. Along this path, understanding of the photophysical processes controlling the MOF/PHI interfacial charge recombination is vital to fine tune the electronic and chemical features of the two components and devise the optimum heterojunction. To address this challenge, we developed a modelling approach integrating force field Molecular Dynamics (MD), Time-Dependent Density Functional Theory (TD-DFT) and Non-Equilibrium Green Function DFT (NEGF-DFT) tools with the aim to systematically explore the structuring, the opto-electronic and transport properties of MOF/PHI heterojunctions conformed by two types of representative 3-D Ti-based MOFs (i.e. MIP-177 and MIL-125-NH_2). We revealed that the nature of the MOF/PHI interactions, the interfacial charge transfer directionality and the absorption energy windows of the resulting heterojunctions can be finely tuned by incorporating Cu species in the MOF and/or doping PHI with mono- or divalent cations. Interestingly, we demonstrated that the interfacial charge transfer can be further boosted by engineering MOF/PHI device junctions and application of negative bias. Overall, our generalizable computational methodology unraveled that the performance of CO_2RR/OER photoreactors can be optimized by chemical and electronic tuning of the components but also by device design based on reliable structure-property rules, paving the way towards practical exploitation.

This work has been financed by the European Union's Horizon 2020 Research and Innovation Program through the MOF2H2 (GA No. 101084131) and METHASOL (GA No. 101022649) projects.