



JOURNÉE DE L'ÉCOLE DOCTORALE S3M – RENNES 2023

ASSEMBLY, STRUCTURE AND ORGANISATION TOWARDS MOLECULAR AND MATERIALS SCIENCE

PLENARY CONFERENCES:

"Polypeptides: from thermoresponsive proteins to new approaches in polymer synthesis"

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Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux

"Control of the hierarchical organization processes between complementary building blocks by irreversible Self-Assembly"

FRANCK ARTZNER

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ROUND TABLE:

"Golden rules to follow during the PhD and further career opportunities"

Université de Rennes
Campus de Beaulieu - Building 2A

25/05/2023

COLLEGE SCIENCES DE LA MATIERE
DOCTORAL DES MOLECULES
BRETAGNE ET MATERIAUX



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INTRODUCTION

Each year, the S3M Doctoral School Day (JED) is a main moment of scientific sharing and conviviality for all Science of Matter, Molecules and Materials Doctoral School (ED S3M). For the first year, the ED S3M gathers scientific people from Rennes and Brest.

This day is the opportunity for doctoral students to meet and discuss their scientific work carried out within the ED S3M. The participation of the greatest number is therefore desired to allow each doctoral student to open to other topics, and to get training and information for his future professional life, with the help of: plenary conferences, oral communications, poster presentations, and a round table.

To embody all the doctoral school subjects, the theme for the JED 2023 is:

“Assembly, structure and organization: towards molecular and materials science”

Like each year, the organizing committee of the JED consists of doctoral students willing to work on this event months before the D-Day, but also on the D-Day, and therefore to give the opportunity to all doctoral students to share their work in the best conditions:

Denis ARI

Alexy BRUNEL

Vanessa DELAHAYE

Elodie DUREAU

Paulina Alejandra MONTAÑO GONZALEZ

Silvia Argelia PERAZA KU

Manon ROCHEDY

Gwendal UGUEN

Ugur Mert ULUTANIR

But this day couldn't take place without the precious help of the ED S3M: we would like to deeply thank Sophie TOMASI, François LIQUE and Nolwenn TUNIER for all the precious advice and all the meetings.

Moreover, the JED wouldn't look the same without the financial support of all our sponsors...

SPONSORS

A huge thank you to all our sponsors!



GENERAL PROGRAM

08h30	Welcome
09h00	Welcome Speech & Sponsors presentation
09h15	Plenary conference - Colin BONDUELLE Amphitheater B
9h50	Oral communications (Amphitheatres B & C)
10h20	Coffee break
10h50	Oral communications (Amphitheatres B & C)
11h50	Lunch break
13h15	Plenary conference - Franck ARTZNER Amphitheater B
13h50	Oral communications (Amphitheatres B & C)
14h20	Poster session + Coffee break
15h40	Oral communications (Amphitheatres B & C)
16h30	Round table Amphitheater B
17h15	Awards and closing ceremony
17h30	Closing cocktail

ROUND TABLE

Golden rules to follow during the PhD and further career opportunities

Dr. Quentin LENNE

Associate Professor - Université Paris Cité

EDS3M graduated

Dr. Aël CADOR

ATER - ENSCR - "Theoretical Inorganic Chemistry" (CTI) team

Dr. Radoslaw DESKA

Post-doctorant - IPR - Materials and light department

Dr. Marius HERVE

Post-doctorant - IPR - Materials and light department

Dr. Solène Guiheneuf-Vacher

Researcher – Kemiwatt company

PROGRAM OF AMPHITHEATER B

Schedule	Speaker	Abstract's title	Booklet page
Welcome speech + sponsor presentation			
9h15	Plenary conference - Colin BONDUELLE <i>Polypeptides: from thermoresponsive proteins to new approaches in polymer synthesis</i>		
9h50	Fatima ZOHRA CHARIK	Analysis of transmissions of charged organic solutes' mixtures in reverse osmosis of brackish and sea waters	14
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10h50	Laurence FERMON	Investigating the mechanisms of action of toxins from <i>S. aureus</i> toxin-antitoxin systems	16
11h05	Christian DEL VALLE VELASCO	Validation of a P precipitation extension model for ADM1: a case study of Valdimeta, pilot-scale anaerobic digester in St-Gilles, France	17
11h20	Nada HAMROUNI	Physicochemical and biological characterizations of by-product, bioactive glass and nano bioactive glass for bone tissue engineering	18
11h35	Solène DUCARRE	Interaction of gold nanoclusters with membranes for labeling and encapsulation	19
Lunch			
13h15	Plenary conference - Franck ARTZNER <i>Control of the Hierarchical organization processes between complementary building blocks by irreversible Self-Assembly</i>		
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14h05	Guilhem PIGNOL	Use of Ferrocenyl functionalised Gold Nano-Particles as a mediator for Scanning ElectroChemical Microscope analysis	21
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17h15	Awards and closing ceremony		

PROGRAM OF AMPHITHEATER C

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Assembly, Structure and Organization
Towards Molecular and Materials Science

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ABSTRACTS OF PLENARY SPEAKERS

Colin BONDUELLE



Colin BONDUELLE is a CNRS researcher working at the LCPO (Laboratoire de Chimie des Polymères Organiques) in Bordeaux. He is a biochemist by training, and did his PhD thesis in polymer chemistry to become an expert in ring-opening polymerization. He currently works on the synthesis, characterization and application of protein-like polymers towards macromolecular therapeutics, nanomaterials/nanocomposites and bioactive scaffolds.

Polypeptides: from thermoresponsive proteins to new approaches in polymer synthesis

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Abstract

Proteins are natural polymers that have many features still unrivaled by their synthetic counterparts, including hierarchical structure, catalytic activity, programmed system dynamics, etc. Compared to proteins, peptidic polymers are much simpler macromolecules in which amino acids are statistically repeated. However, those polypeptides combine advantageous features of synthetic polymers (solubility, process, rubber elasticity, etc.) with those of natural proteins (secondary structure, functionality, biocompatibility, etc.). [1]

The most efficient route to polypeptides is a polymer synthesis: the ring-opening polymerization (ROP) of amino acid N-carboxyanhydride (NCA) monomers (figure 1).[1,2] Recent progresses in NCA chemistry have been impressive: efforts have focused on promoting the polymerization without the use of a catalyst, exploring more reactive initiators, and using heterogeneous processes including aqueous media.[3] In this context, this talk will illustrate how polymerization of NCA can afford simplified analogues of thermoresponsive proteins exhibiting unprecedented LCST.[4]

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4. C. Bonduelle et al. *Angew. Chem. Int. Ed.* **2022**, *61*, e202209530.

Franck ARTZNER



Franck ARTZNER is a CNRS researcher working at the IPR (Institut de Physique de Rennes) in Rennes. He is the leader of the “Biomimetic self assemblies” group at the IPR. He is an expert in bio-inspired materials with applications in oncology and cosmetics. He supervised two PhD students : Charlène HUBERT (long-lasting performance of make-up products) and Arnaud BARDOUIL (self-assembled materials).

Control of the Hierarchical organization processes between complementary building blocks by irreversible Self-Assembly

Abstract

Large structures are generally built-up by combining several complementary materials. For example, skyscrapers are thus built by adding an inorganic material, concrete, around an scaffold. This duality is found in all natural inorganic structures such as bones, naces, or marine organisms skeletons based on silica. These materials are composite phases based on polymers (proteins, etc.) and inorganic nanocrystals.

In terms of construction, in the case of skyscrapers, the project manager organizes the sequential and alternative arrival of concrete and iron bar. For natural structures, controlling the self-assembly process is still an open question. Through several examples studied for 20 years by doctoral students from the material doctoral school of Rennes, we will see how it is possible to identify simple rules of self-assembly allowing to control simple morphologies from the nanometer to the centimeter.

Papers with Doctorants from ED S3M:

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MT 180 Videos :

Arnaud Bardouil : <https://m.youtube.com/watch?v=q5R0qSHthLk>

Charlène Hubert : <https://m.youtube.com/watch?v=BvF0cehYjVc>

ABSTRACTS OF ORAL COMMUNICATIONS

Analysis of transmissions of charged organic solutes' mixtures in reverse osmosis of brackish and sea waters

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Abstract

Sea water Reverse osmosis (SWRO) membranes were designed for the inorganic salts' rejection, but recently partial transmission of small organic solutes ($MW \leq 200 \text{ g.mol}^{-1}$) was evidenced, which is a new challenge to face during the desalination of polluted seawater. These behaviors underline that solute MW and size are far from being the single accounting parameters to understand the rejection mechanism of organics in RO.

Besides the role of the native defects inside the "dense" polyamide membrane, the literature data raise the question addressed in this study: where is the real limit of a charged solute transmission through SWRO membrane with respect to its MW and to physico-chemical interactions in the membrane/solute/seawater system?

To answer, 4 model organic solutes have been filtered in cross-flow conditions in either deionised water, 30 g.L⁻¹ NaCl, or seawater (pH 7.5-8.2) using the SW30 membrane (Filmtec) in the 30-40 bar applied pressure range.

A set of azo-dyes and a vitamin (254 to 854 g.mol⁻¹) is selected, moreover covering a wide range of properties (positive and negative charges, variable hydrophobicity $\log Kow = -2.55$ to $+4.96$). The solutes set at 0.5 mmol. L⁻¹ each were filtered either in single, binary and ternary mixtures to consider the possible impact of solute/solute interactions on the transfer mechanisms.

Regardless of the environment, all the solutes were slightly transmitted through the membrane. In presence of ionic strength (NaCl or seawater), the transmission of charged organic solutes depends on the solute-membrane hydrophobic interactions. In double and triple-organic solute systems, the respective hydrophilicity of each solute plays a significant role in the transmission. This study provides a more in-depth discussion of the physico-chemical parameters accounting for the transfer through the membrane.

Liquid phase synthesis and application of sulfide solid electrolyte

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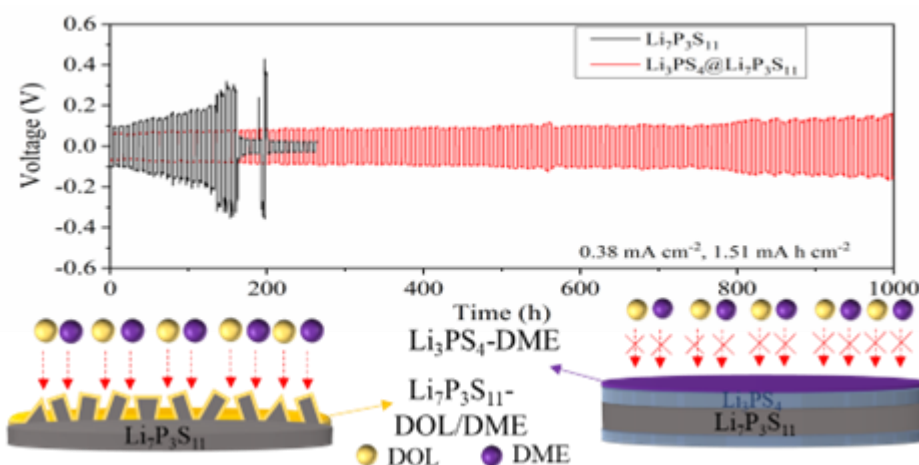
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Abstract

Lithium-sulfur (Li-S) batteries are considered a promising next-generation energy storage system due to their high theoretical energy density (2600 W h kg⁻¹), abundant and low cost sulfur resources on earth. [1] [2, 3] Over the past few decades, though many studies have been reported, Li-S batteries still have some serious problems. [4] [5] In conventional organic liquid electrolyte systems, there will be parasitic reactions between the Li anode surface and organic liquid electrolytes. The cathode will generate lithium polysulfide (LiPS) in liquid electrolytes. The LiPS can lead to “shuttle effect” in liquid electrolytes, resulting in low Coulombic efficiency and battery safety issues.

The Solid/liquid Li-S battery shows promise in solving both the polysulfide “shuttle effect” in liquid batteries and the interfacial contact in all solid-state batteries. However, increasing the interfacial stability of the electrolyte and the solid electrolyte remains a challenge in the solid/liquid batteries. In this work, a high ionic conductivity Li₃PS₄ solution is synthesized using a nano-Li₂S precursor, which is then utilized to form a solid electrolyte Li₃PS₄@Li₂P₃S₁₁ via dip-coating. The high stability of Li₃PS₄@Li₂P₃S₁₁ with the DOL/DME and DME electrolyte is demonstrated. The lithium symmetric battery with the solid electrolyte Li₃PS₄@Li₂P₃S₁₁ is cycled stably for 1000 h, under a current density of 0.38 mA cm⁻² and a capacity of 1.51 mA h cm⁻². The Li-S battery with the solid electrolyte Li₃PS₄@Li₂P₃S₁₁ can cycle stably for 300 cycles at 0.2 C with a capacity of 600 mA h g⁻¹ remaining.



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**Investigating the mechanisms of action of toxins from *S. aureus*
toxin-antitoxin systems**

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Abstract

Toxin-antitoxin systems are genetic modules widely spread in bacterial genomes. They contain a toxin, which stops the bacteria's growth and an antitoxin, which inhibits toxin's expression. Under normal conditions, the antitoxin is produced concomitantly with the toxin, so the toxin is not translated. Under a stress, the antitoxin is not produced anymore, so the toxin can be translated, acts on the bacteria and stop its growth when produced in high quantity. The role of these systems is still elusive. So far, they have been shown to be involved in the maintenance of mobile genetic elements, growth adaptation to environmental stresses or antibiotic persistence.

Staphylococcus aureus is a major human pathogen and one of the first cause of hospital-acquired infections. Several type I toxin-antitoxin systems have been discovered in *S. aureus* genome. These systems are thought to be involved in *S. aureus* pathogenicity and antibiotic persistence.

Notably, three of *S. aureus* type I toxins have been studied [1-3]: these toxins are small cationic peptides structured in alpha helix. They show hemolytic activity against erythrocytes, while they do not exhibit effective antibacterial activity. How to explain this specificity of action?

We aim here to investigate their structures and the interactions with membranes when overexpressed inside the bacteria. We also study interactions with model membranes in order to gain insight about the selectivity of these toxins for mammalian versus bacterial cell membranes and so about their biological roles and mechanisms of action.

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Validation of a P precipitation extension model for ADM1: a case study of Valdimeta, pilot-scale anaerobic digester in St-Gilles, France

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Abstract

Anaerobic Digestion Model N°1 (ADM1) has been widely used in developing and optimizing anaerobic digestion (AD) in the last 20 years. Although ADM1 was initially conceptualized based on carbon balance, intensive research has been conducted to improve other nutrient flows linked to AD, notably for nitrogen (N), to investigate the fertilizer potential of digestate, the main AD by-product after biogas. However, after N, phosphorus (P) content in digestates has been targeted in several studies as a key source for P recovery to face the current unsustainable P management. P dynamics within AD are primarily found in solid and liquid phases. Factors such as pH, temperature, and the presence of other nutrients (e.g. calcium, potassium, iron, aluminum) help to determine if P is in phosphate form (soluble) or one of the P-rich minerals (precipitated) that can be found in the digestate. Chemical speciation and ion pairing that govern P dynamics are not included originally in ADM1. Therefore, an extension to model P precipitation is needed to improve P management from digestate.

We constructed a precipitation model considering solubilization and precipitation processes for several minerals identified in digestate that can impact P dynamics (e.g. struvite, calcite, vivianite, ...). Since saturation is a crucial factor behind precipitation and dissolution mechanisms, saturation indexes (SI) were calculated by combining ADM1 with PhreeqC, a geochemistry software. ADM1 provides the necessary information to PhreeqC for the chemical speciation and SI calculation, which ADM1 uses to calculate precipitation or dissolution rates. By combining both models, mineral precipitation or dissolution is calculated. The whole model was calibrated using parameters from the literature, and a sensitivity analysis was conducted to identify the most sensitive parameters.

Finally, we used experimental data from Valdimeta, a 15 m³ anaerobic digester fed with pig slurry in St-Gilles, France. Results from these experimental trials combined with the knowledge from sensitivity analysis were used for model validation. Results obtained from our model include carbon and nitrogen behavior, biogas production, and mineral precipitation/dissolution based on P. Finally, our model was validated for predicting P behavior throughout AD in Valdimeta.

Physicochemical and biological characterizations of by-product, bioactive glass and nano bioactive glass for bone tissue engineering

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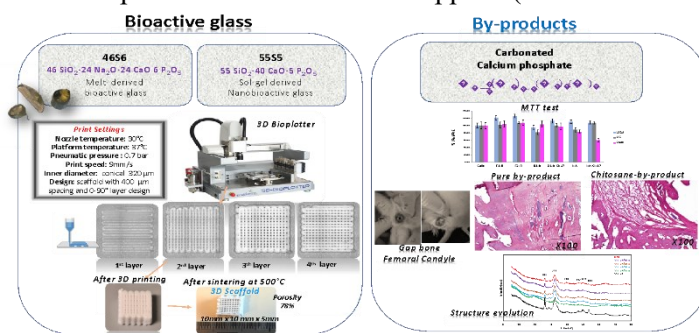
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Abstract

My thesis was structured into two primary segments, both of which were related to the development of biomaterials aimed at being utilized in bone tissue engineering applications. In the first part, we focused on the synthesis and characterization of various biomaterials, namely Melt derived bioactive glass **46S6** and sol-gel derived nanobioactive glasses **55S5** for applications in orthopaedic surgery and osteoporosis treatment. The physicochemical and biological properties of each biomaterial were comprehensively evaluated and compared. The ultimate aim of this investigation was to develop suitable pure biomaterials and associated **chitosan**. A new fourth-generation printer, the '**3D Bioplotter**', which we acquired in our research group, was used to fabricate 3D scaffolds. This is a very promising approach in tissue engineering, as it allows for automated fabrication using computer-controlled scaffolds with precisely controlled porosity characteristics. Furthermore, the micro- and nanostructures promote adhesion between osteoblasts and the scaffold. In the second part of the study, we aimed to explore the potential valorisation of natural **by-products** in collaboration with Abyss ingredients and Cooperl innovation companies *. To this end, we examined the feasibility of using these by-products as a raw material and evaluated the performance of the resulting materials **in vitro and in vivo**. As a result of the research conducted with Abyss ingredients, a **patent** (reference number FR2206238) was filed for the use of fish by-products as biomaterials in bone regeneration, indicating successful valorisation of this work. Similarly, in vitro tests with immersion in synthetic physiological fluid (SBF) and in vivo experiments in femoral condyles of rats after creating osteoporotic by using ovariectomy process were performed. This allowed us to highlight these different behaviours. New bone formation and the treatment of induced osteoporosis were followed over time after immersion for in vitro experiments and after implantation for in vivo experiments. A new project with Cooperl Innovation company is in the way.

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Interaction of gold nanoclusters with membranes for labeling and encapsulation

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Abstract

According to their high electron density and ultrasmall size, gold nanoclusters (AuNCs) have unique luminescence and photoelectrochemical properties that make them very attractive for various biomedical fields. These applications require a clear understanding of their interaction with biological membranes to enhance their biocompatibility and delivery efficiency.

We demonstrate the ability of the AuNCs as markers for lipidic bilayer structures such as synthetic liposomes and biological extracellular vesicles (EVs). The AuNCs can selectively interact with liposomes or EVs through an attractive electrostatic interaction as demonstrated by zetametry and fluorescence microscopy. According to the ratio of nanoclusters to vesicles, the lipidic membranes can be fluorescently labeled without altering their thickness until charge reversion, the AuNCs being located at the level of the phosphate headgroups. In presence of an excess of AuNCs, the vesicles tend to adhere and aggregate. The strong adsorption of AuNCs results in the formation of a lamellar phase as demonstrated by cryo-transmission electron microscopy and small-angle X-ray scattering techniques.^[1]

In addition, the high colloidal stability of the C3E6D NC and their ultra-small size makes possible to encapsulate the C3E6D NC into synthetic liposomes (GUVs, LUVs, SUVs) with a high efficiency by preserving the bilayer integrity and the vesicle morphology.^[2]

So these ultra-small and stable gold nanoclusters can serve as biomarkers of lipidic membranes such as EVs; furthermore liposomes encapsulation can serve as cargo to bring Au NCs into cells or EVs for in-situ biosensing or drug delivery.

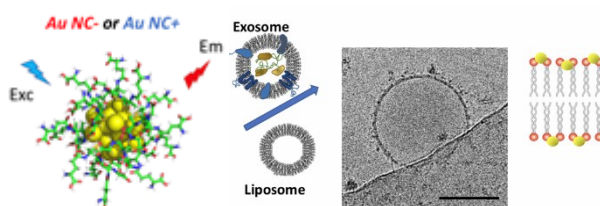


Figure 1: (a) Scheme of the gold nanoclusters, (b) Interaction with liposomes or exosomes

Chiechio, R. M. et al. Luminescent Gold Nanoclusters Interacting with Synthetic and Biological Vesicles. *J. Phys. Chem. Lett.* **2022**, 13 (30), 6935–6943. <https://doi.org/10.1021/acs.jpcllett.2c01071>.

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Emulsion processing of gold nanoparticle shells: towards plasmonic nanoresonators

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Abstract

The chemistry of metallic nanoparticles, and more specifically that of noble metals, is a rapidly expanding field (1). The elaboration of well-ordered assemblies of nanoparticles by solution routes remains an experimental challenge, with a wide potential of applications. In the case of metallic gold or silver nanoparticles, electromagnetic effects resulting from plasmonic coupling between the nanoparticles are expected. In particular, "hollow" spherical assemblies of such nanoparticles can constitute plasmonic nanoresonators capable of interacting with the magnetic component of light, a phenomenon that does not exist in natural materials. Such nanoresonators are being considered as the building blocks for the development of metamaterials.

Our team has developed a process for the formulation of nanoparticle shells, based on an unconventional emulsification (spontaneous and without surfactant): The Ouzo effect.(2) This strategy allows the assembly of nanoparticles around droplets of about 100nm in diameter, with excellent size homogeneity. However, this has not been achieved with gold yet.

The objective of this work is to elaborate gold NP shells and to understand the physico-chemical mechanisms involved in order to develop metamaterials and explore their applications.

The first part is devoted to the study of the ternary ouzo system "water/THF/BHT" allowing the formation of NP-shells.(3) In addition, we look at the effect of NP on the drops. Furthermore, the idea is not only to assemble the gold nanoparticles around the ouzo drops but also to control the distance between them by substitutions in situ with shorter ligands in order to have plasmonic coupling, which is necessary to obtain the desired optical properties.

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Use of Ferrocenyl functionalised Gold Nano-Particles as a mediator for Scanning ElectroChemical Microscope analysis

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Abstract

The Scanning Electrochemical Microscope (SECM) in feedback mode allows to probe the different electron exchange that occurs between an active redox species and a surface. The active form of the mediator is formed at a nano or micrometric tip and diffused in the sample in this technique. When the tip come closer to the surface, the mediator active species can interact with the surface. In particular if the surface can exchange electron, a redox loop is formed and the current with the distance will change. Indeed, the usual steady state which is well known will be affected by this electronic loop. In particular, the shape of this curve can provide information concerning the electron exchange kinetics.

Usually, the mediator used in this kind of experience exchanges only one electron per molecule. The use of species in SECM which can exchange multiple electron have been described ten years ago by our group using redox dendrimer and change the view of the sample. (1)

In that context, redox active nanoparticles as those prepared by attaching molecules presenting a reversible electron transfer on their surface, appear as promising systems of specific multielectronic probes for SECM. In this work, we have investigated the use of soluble Fc-AuNps as a redox mediator for the SECM. The basic electrochemical properties of ferrocenyl functionalised Gold Nanoparticles (Fc-AuNps) has been described. The size of the nanoparticles but also the number of attached ferrocenyl ligands as the nature of the supporting electrolyte influence the electrochemical behaviours. (2) SECM responses with such nanoparticles have been compared to the classical ones obtained with classical mediator as ferrocene that could only transfer one electron per molecule.

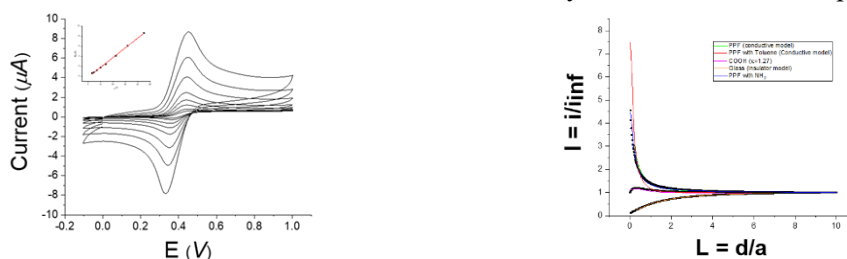


Figure 1: Cyclic Voltammograms obtained for Fc-AuNPs in CH₂Cl₂ using Geiger Salt as supporting electrolyte (left), Probe approach curve obtained on pyrolysed photoresistfilm functionalised with different molecules using as a mediator the Fc-AuNPs (right)

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**Excitation of CS induced by collisions with CO of interest for
cometary applications**

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Abstract

Comets are formed from primitive material at the first stages of the formation of our solar system. As the matter continues to evolve to form planets, it was trapped on cometary ices. Their chemical compositions are therefore a tracer of our early solar system.

To probe chemical and physical conditions on comets (abundance of molecules, volume density of the gas, temperature), molecular spectra captured by telescopes are analyzed. However, this analysis requires collisional rate coefficients, that indicates the probability of excitation of a molecule induced by collisions with another one.

Computing such collisional rate coefficient represents a real methodological and numerical challenge for the astrophysical community. For now, they are limited to small molecules in collision with He or H₂. However, on cometary atmospheres, the most abundant molecules are CO, H₂O and CO₂, and thus, traditional full quantum approach is not reachable, both in terms of memory and computational time.

CS is one of the 200 molecules detected in cometary atmospheres, and one of the 195 for which there is no collisional rate coefficients for these astrophysical media. It was often detected in comets, and is suspected to be formed by irradiation of the cometary ices when they come closer to our sun. However, its formation path is still under discussion. Therefore, the obtention of the rate coefficients of CS in collision with CO will help to obtain its abundance with more accuracy, and thus discuss its formation path.

The collisional rate coefficients for CS-CO are computed within the Born-Oppenheimer approximation, which decouples electronic and nuclear motion. Electronic Schrödinger equation is solved here with the gold-standard CCSD(T) ab initio method, and its analytical expression is obtained as implemented in the AUTOSURF program. The analytical expression of the PES is then implemented in scattering code, and the nuclear Schrödinger equation can be solved.

Since the full quantum scattering approach is not reachable in terms of computational time and memory, we will present here the methodology that we are trying to develop to treat this system, and that can be extended to other collisional systems of cometary interest.

2- μm thulium fiber laser source for supercontinuum generation

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Abstract

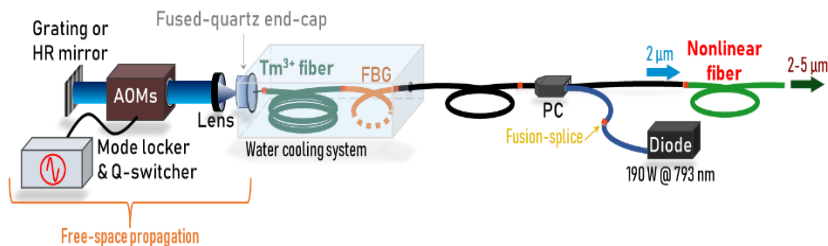
The mid-infrared spectral region is of great technical and scientific interest because most molecules display fundamental vibrational absorptions in this region, leaving distinctive spectral fingerprints, and the potential of fibers to emit across the mid-infrared molecular ‘fingerprint region’ is of key importance for applications such as early cancer diagnostics, gas sensing, food quality control and infrared counter-measures; for this reason, sources of broadband middle-infrared light are currently the subject of active research.

In this field, supercontinuum sources have continuously attracted a great deal of interest because this phenomenon, known as supercontinuum generation (SCG), is one of the most spectacular and visually perceptible nonlinear effects produced by the propagation of intense laser pulses in a transparent nonlinear medium, and allows to deliver a good beam quality while producing a large and relatively flat spectrum over several microns in the mid-infrared (1).

Originating from the spectral broadening of a seed pulse due to a wide range of nonlinear effects such as self-phase modulation (SPM) or Raman effects, the SCG can be generated from different pulse durations and nonlinear materials resulting in different output characteristics: for example an intense (amplified) ultrashort pulse might be sent through a piece of crystal or, alternatively, pulses with much lower pulse energy could be injected through an optical fiber.

Thanks to their waveguide structure, which allows for a long propagation length with small effective mode area, their transparency, compactness and reliability, optical fibers can be considered the best candidate as optical medium. Of high importance is the choice of the fiber glass in order to allow the spectral broadening in the mid-IR: silica ones are not suitable for this scope since they are transparent up to a wavelength of 2.6 μm because of their intrinsic absorption. The most common and mature developed fibers which fit the requests belong to the fluoride and chalcogenide families (2).

In this study, a pulsed thulium fiber laser source emitting around 2 μm is investigated to realize a pump source that allows the efficient generation of infrared supercontinuum in the spectral range 2-5 μm , with an average power of about ten watts in “single-step” or in a non-linear fibers cascade.



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Surface passivation characteristics of III-V elements on Si (001)
substrate using Density Functional Theory

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Abstract

Keywords: Density Functional Theory, surface energy, barrier energy, nudged elastic band, III-V/Si epitaxy.

Although it has been a long-standing difficulty, integrating III-V compound semiconductors on Si (001) substrates presents a chance to considerably reduce the cost of producing many devices. It is possible to better comprehend heterogeneous epitaxy and wetting-property research by having a solid understanding of surface passivation technique [1-4]. In this study, we investigate the surface passivation behavior of III-Vs on Si, compute the absolute surface energies and barrier energies (nudged elastic band method) for III-V monolayer interactions with the Si (001) surface, and analyze the results. Using the density functional theory simulations, we provide quantitative evidence that the nature of the monoatomic layer formed on the substrate surface has a significant impact on the general description of surface passivation, wetting properties, and epitaxial growth.

This research was supported by the French National Research NUAGES Project (Grant no. ANR-21-CE24-0006). DFT calculations were performed at Institut FOTON, and the work was granted access to the HPC resources of TGCC/CINES/IDRIS under the allocation 2022-A0120911434 and 2023-A0140911434 made by GENCI.

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Rational Design of Carbon-Supported Tungsten Carbide Electrocatalysts for pH-Universal Hydrogen Evolution Reaction

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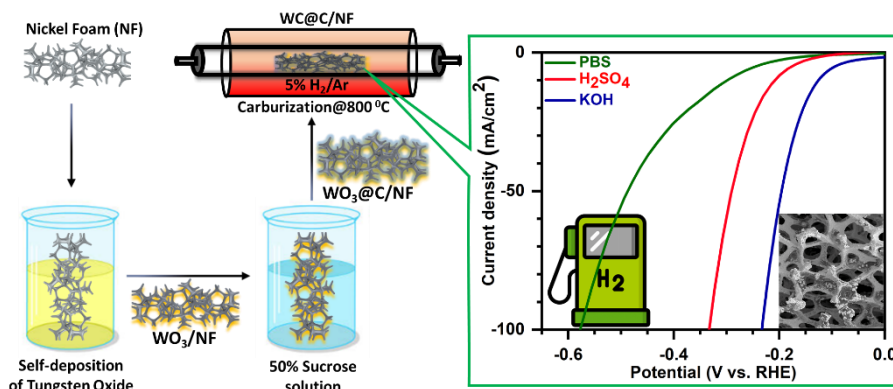
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Abstract

Dihydrogen (H_2) is a clean energy carrier and sustainable alternative to traditional fossil fuels for meeting future energy demands. However, around 95% of global H_2 comes from the steam reforming process which leads to the emission of greenhouse gases. Electrochemical water splitting is a promising approach to produce eco-friendly H_2 involving a hydrogen evolution reaction (HER) at the cathode and an oxygen evolution reaction (OER) at the anode, utilizing renewable energy sources such as wind or solar power.¹ In recent years, remarkable efforts have been made to replace expensive noble metal-based electrocatalysts (Pt/Pd for HER and IrO_2/RuO_2 for OER). Transition-metal carbides (TMCs) have been explored as alternatives, particularly tungsten carbide (WC) is known for its Pt-like catalytic properties due to similar d-band electronic density of states and has been explored as earth-abundant alternative electrocatalysts for HER in both acid and alkaline conditions.²

Herein, we
on a facile
approach
prepare
supported



electrocatalyst on nickel foam (NF) from the thermal reduction of a sucrose-impregnated self-deposited tungsten trioxide (WO_3) precursor.³ The optimal electrocatalyst ($WC@C/NF$), exhibiting the best electrocatalytic efficiency was obtained from the precursor impregnated with 50% sucrose and thermally reduced at $800^\circ C$ under H_2 atmosphere. $WC@C/NF$ requires low overpotentials of 0.124, 0.208, and 0.298 V to achieve a current density of -10 mA/cm^2 in alkaline, acidic and neutral pH respectively and stable for 40 h. The presence of excess amorphous carbon embedding WC is beneficial to improve the conductivity and the dispersibility of the electrocatalyst, and consequently its HER activity. Our findings demonstrate that binder-free WC-based HER electrocatalysts can be produced easily from self-deposited WO_3 film and sugar as the carbon/carbide source.

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Charge Transport of Electroactive Ferrocene-functionalized MoS₂

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Abstract

Since the isolation of graphene monolayers,^[1] two-dimensional (2D) materials have emerged as promising nanostructures for numerous applications ranging from electrocatalysis, optics to electronics. Among these materials, transition metal dichalcogenides (TMDs), such as MoS₂, have been widely studied. Depending on their polymorphic structural features, these materials exhibit either semiconducting or metallic properties increasing the interest for their usage in electronics, such as high-performance field effect transistors (FETs) and diodes.^[2] The attachment of molecular units to these 2D nanomaterials, mainly concerning MoS₂, in order to finely tune their physicochemical properties and confer them novel functionalities has attracted great attention over the last two decades. Although major advances in device's performance, such as FETs, through molecular functionalization have been reported, the grafting of redox-active molecules has been only marginally explored.^[3] In particular for the purpose of designing electrochemically switchable devices, the control of the material's charge/spin transport properties by the redox state of the grafted molecule and thus the applied electrical potential has yet to be fully investigated. In that context, the Samori's group has nicely reported on the novel ferrocene-functionalized MoS₂-based field-effect transistor (FET) architecture.^[4]

In this work, the functionalization of MoS₂ with ferrocene (Fc) was revisited and a deeper knowledge of this material was gained by combining multiple surface characterization techniques including μ -Raman, μ -photoluminescence, X-ray photoelectron spectroscopies and atomic force microscopy (AFM). The effect of the attached electroactive molecular unit was studied by conducting AFM to determine the energy bands alignment at the MoS₂-Fc/metal interface, a prerequisite for their employment in electrochemically switchable devices. Detailed electrochemical investigations of these redox-active interfaces, using cyclic voltammetry, provided key insights into the charge transfer mechanism of these nanostructured assemblies.

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Synthesis and complexation of n-unsubstituted unstable imines

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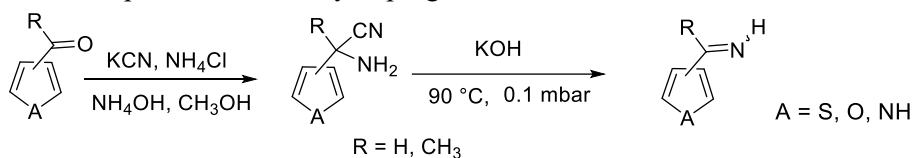
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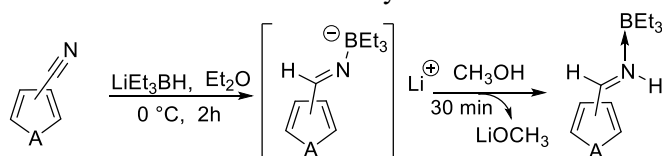
Abstract

N-H aldimines are compounds that are often kinetically very unstable but which play a decisive role in organic chemistry, generated in situ in Mannich or Strecker reactions or, in the form of iminium, in Diels-Alder cyclizations.¹ Imines which are dimers of hydrogen cyanide could have played a determining role in the formation of prebiotic compounds on the Primitive Earth.² It is interesting to isolate such species and to characterize them by spectroscopy. This made it possible in particular to detect five of them in interstellar clouds.³ They thus constitute one of the main heteroatomic groups of this medium, however far behind the nitriles.

We herein report a preparation of N-H imines associated to a furan or thiophene substituent (which possess different levels of aromaticity) in the aim to have a better knowledge of such compounds, to study the formation of complexed derivatives and the chemistry on the both forms. Imines are synthesized in a two-step sequence starting from the carbonyl derivative involved in a Strecker reaction and followed by a dehydrocyanation by vaporization of the α -aminonitriles onto powdered KOH (Scheme P1).⁴ Attempts to form complexes by addition of triethylborane failed but they were obtained from the corresponding nitrile and superhydride (LiEt₃BH) (Scheme 2).⁵ All synthesized products are characterized by ¹H and ¹³C NMR spectroscopy, infrared spectroscopy and mass spectroscopy. The extension of this work to pyrrole derivatives and to the study of the chemical reactivity of all these compounds is currently in progress.



Scheme 1 : Synthesis of imines



Scheme 2 : Preparation of Imine-Triethylborane Complexes

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Synthesis and photophysical studies of enantiopure cycloplatinated pentahelicenic N-heterocyclic carbenic complexes

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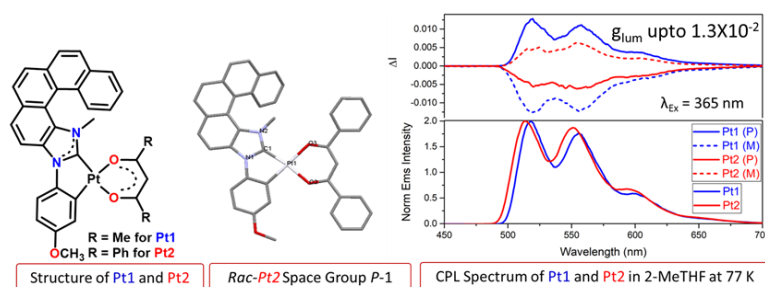
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Abstract

Circularly polarized luminescence (CPL) emitters have gained significant research attention for their potential applications in advanced optical technologies like optical data storage, telecommunication, and stereoscopic 3D imaging systems.¹ One promising class of compounds for Light emitting diode applications is platinum N-Heterocyclic Carbene (Pt-NHC) complexes, which are known for their heavy metal spin-orbit coupling, high phosphorescence quantum yield, and exceptional photostability.² To develop novel chiral platinum complexes that can emit CPL with both high photoluminescence quantum yield (F) and dissymmetry factors (g_{lum}),³ we synthesized photostable helicene-based NHC-Pt systems (Pt1 and Pt2) and explored their photophysical and chiroptical properties. Our findings showed that although these new complexes exhibited moderate CPL response at room temperature (up to 3×10^{-3} for Pt1) both in solution and films, they displayed strong CPL response at 77 K (g_{lum} up to 1.3×10^{-2} for Pt1).⁴ Furthermore, the moderate quantum yields and robust chiroptical properties of Pt complexes make them suitable for developing CP-OLED devices. In summary, our study highlights the potential of helicenic Pt-NHC derivatives as promising candidates for advanced optical technologies.



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New routes towards helical thioxanthone-based hexacycles

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Abstract

Helical molecules are widely present in nature. Besides DNA which is probably the most known double helix structure, alpha-helices can also be found in many proteins. Our laboratory has previously prepared benzothieno[2,3-*b*]benzothiopyrano[4,3,2-*de*]quinoline (Figure 1, left, X = S), a fluorescent helicene-like polycyclic, heteroaromatic molecule that proved to be a promising inhibitor of disease-related PIM protein kinases.¹ This work focuses on a safer way to reach this compound and related aza analogues.

The synthesis of our key intermediate 1-aminothioxanthone was achieved in four steps and in 32% overall yield from commercially available thioxanthone. First, 1-iodothioxanthone was obtained by deprotolithiation and *in situ* transmetalation-iodolysis of the bare heterocycle. The amino group was next introduced by Gabriel's reaction involving copper-mediated *N*-arylation with phthalimide. While the tandem *N*-arylation/cyclisation appeared to be favoured by the absence of sulfur bridge, 2-iodo-*N*-methylindole gave higher yield than 2-iodobenzothiophene. Our efforts were next concentrated on the synthesis of benzofuro-, benzothieno- and 10-methylindolo- [2,3-*b*]benzothiopyrano[4,3,2-*de*]1,8-naphthyridines which are original hexacycles also endowed with interesting fluorescence properties. These compounds were further evaluated as originals and highly fluorescent inhibitors of Pim kinases related to cancer development, and the results were rationalized by molecular modelling experiments².

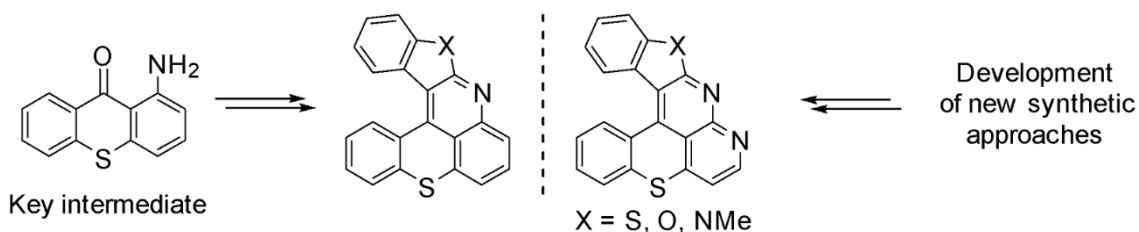


Figure 1: Structures of benzothieno-, benzofuro-, 10-methylindolo-[2,3-*b*]benzothiopyrano[4,3,2-*de*]quinolines (left) and -[2,3-*b*]benzothiopyrano[4,3,2-*de*]1,8-naphthyridines (right)

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Patterning Organic Layers on Carbon Surfaces using Electro-labile Protected Aryl Diazonium Salts

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Abstract

The reduction of aryl diazonium ions leads to aryl radical formation concomitant with the loss of N₂. The high reactivity of aryl radicals allows for the rapid (seconds to minutes) grafting of aryl moieties onto the surface of interest. This leads to robust and versatile grafted films. [1] The technique has been used for many applications from sensors and biosensors to active plasmonic devices. [2] In order to realise the full potential of aryl diazonium grafting, new strategies are needed. For instance, researchers have proposed several methods to pattern these films. One of the first approaches was to use methods developed for other modifiers, mainly self-assembled monolayers (SAMs), such as inkjet printing, micro-contact printing (μ CP) or nanosphere lithography. Surface probe microscopy (SPM) has also been used to pattern such substrates, as scanning electrochemical microscopy (SECM) to locally generate aryl radicals from aryl diazonium salts in order to pattern carbon surfaces. [3]

Here we propose the synthesis and use of a new aryl diazonium salt bearing an electro-labile protecting group. After grafting to a carbon electrode, the protecting group is deprotected *in situ*, leading to the formation of a reactive benzoic acid layer that can be easily post-functionalized through carbodiimide coupling in order to graft a wide range of (bio) molecules. Moreover, using scanning electrochemical cell microscopy (SECCM) it is possible to pattern such organic layers on electrode surfaces.

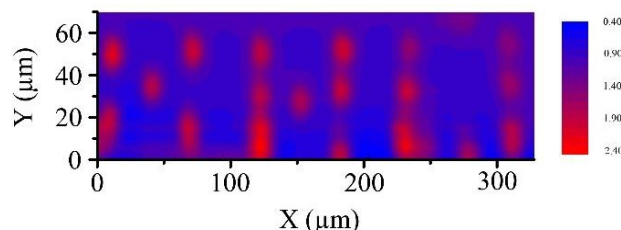


Figure 1. SECM image recorded with dopamine (1 mM) in 0.1 M H₂SO₄ solution, after patterning organic film generated by the electroreduction of aryl diazonium salt bearing electro-labile protecting group, with scanning electrochemical cell microscopy (SECCM) a “XMU” motif.

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Highly ordered assemblies of helicenes with phase-segregated siloxane block oligomers for CPL emission

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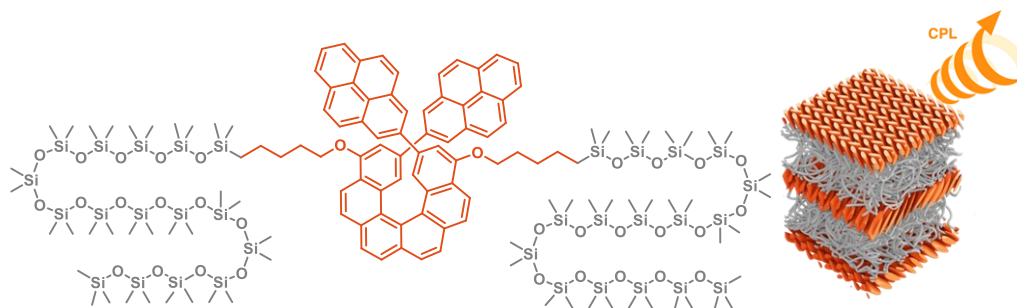
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Abstract: (Your abstract must fit in this box and should use Times New Roman (Font size 10). Your abstract should be no longer than 250 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Helicenes are chiral molecules constituted by ortho-condensed polycyclic aromatic rings. They show great potential as chiroptical materials because they present elevated electronic circular dichroism (ECD) activity but low circularly polarized luminescence (CPL) emission. Synthetic strategy, like incorporating into the helicene a metallic centre¹ or adding a chromophore spaced by a triple bond² leads to an improvement of the photophysical and chiroptical properties of this class of molecules.

The direct modification of the molecular structure is not the only way to control the properties of the materials; self-assembly can also play an important role. One way to control the self-assembly is to couple an organic molecule with discrete dimethylsiloxane oligomer; these systems are constituted by a “hard” molecular core and “soft” siloxane chain. The small volume fraction of the siloxane chain can allow a small size ordered domain with less defect, also, directional interaction between molecules can give rise to the formation of complex structures with unique properties³.

In this work, we report the synthesis and optical properties of a new class of helicene compounds coupled with discrete dimethylsiloxane oligomers. The relationship between self assembly ordering and CPL activity will be discussed. Self-assembly studies were investigated in collaboration with the Meijer's group from the Eindhoven University of Technology, Netherland.



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**All-Inorganic Luminescent Solar Concentrator based on
Transparent Multicomponent PbSe QDs Glasses**

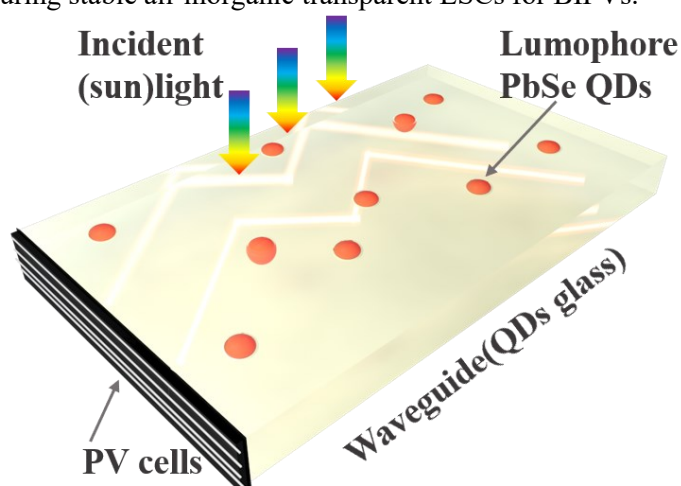
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Abstract

Luminescent solar concentrators (LSCs) have important application in building integrated photovoltaic systems (BIPVs)¹. Quantum dots (QDs)-embedded glass, which is a specific type of glass ceramics that do not participate in the crystallization of the network formers, has the combined advantages of excellent optical properties of QDs and easy processing of glass². In present work, the suitability of inorganic PbSe QDs glasses for use in LSCs as both transparent matrix and lumiphore, as an alternative to the combination scheme of environmentally sensitive colloidal QDs or organic dyes and aging-prone organic polymer materials is demonstrated. The inorganic PbSe QDs glass developed exhibited a strong UV absorption, large Stokes shift, broadband excitation and emission, and high transparency in the visible range. Coupled with the silicon solar cell, the as-prepared transparent LSC based on PbSe QDs glass exhibited an optical efficiency of 10.13 % and a power conversion efficiency of 1.59 % under standard sunlight. These results demonstrate a new strategy for manufacturing stable all-inorganic transparent LSCs for BIPVs.



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Photothermal metal-bis(dithiolene) complexes as anticancer drugs

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Abstract

Some molecules and materials can efficiently convert light into heat, which is called the photothermal effect (whose efficiency can be quantified by the photothermal yield η). This property can be exploited to kill tumorous cells, especially in the near-infrared (NIR) biological window (700 – 1850 nm) where the light penetration depth, dispersion and autofluorescence is the lowest¹. However, the tumor site does not intrinsically possess enough photothermal molecules and exogenous photothermal agents (PTAs) must be introduced into the tumour site.

Metal-bis(dithiolene) complexes are known for their strong absorption in NIR window, easily modulated in intensity and wavelength of maximum absorption, by the choice of the metal and the ligands². In this work, we focus on nickel, palladium, platinum and gold-bis(dithiolene) complexes functionalized with long carbon chains. Although they show great photophysical properties ($\epsilon \sim 105$ L/mol.cm and $\eta \sim 45\%$), their hydrophobicity makes it impossible to use them in biological media without an appropriate formulation. So, our team conceived, designed and prepared nanoparticles (NPs) of biocompatible and biodegradable polymers^{3,4}, to encapsulate these complexes. The resulting suspensions of polymeric NPs encapsulating metal-bis(dithiolene) complexes show high reproductibility of preparation and stability of at least one month at 5°C. Recent *in vitro* and *in vivo* studies on breast cancer cells and zebrafish embryos performed under laser irradiation at 880 and 940 nm, at different power per surface unit, show that these NPs are promising PTAs for photothermal therapy.

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Organolanthanide complexes: ab initio electronic structures investigation and magnetic properties rationalization

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Abstract

Single Molecule Magnets (SMMs) are widely studied because of their potential impact in applications such as high-density information storage, quantum computing or spintronics.¹⁻⁴ Organolanthanide complexes are a great way to design performing SMMs. However, enhancing the magnetic properties of Ln based SMMs, that is, getting compounds with a slow magnetic relaxation and the highest blocking temperature possible, is a major challenge.⁵

In this work, different design strategies for organolanthanide SMMs are computationally explored, such as the use of cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) large ligands, radical-bridged ligands, or even the seek for a diffuse valence orbital between two lanthanide centres. Recent computational and magnetic measurement results on Ln-Cnt complexes, compounds based on radical-bridged ligands, and derived, will be presented.⁶⁻⁸

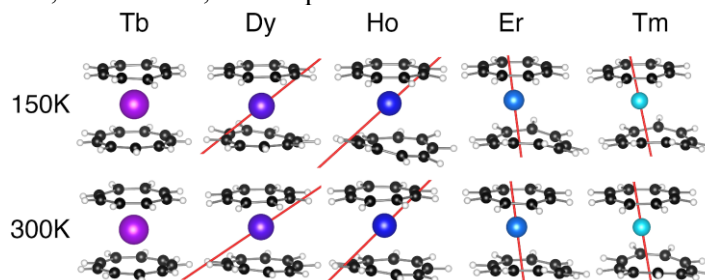


Figure: Computed structures of Dy(Cnt)₃ (left), [(Cp*₂Dy)₂(μ-Bbim•)]⁻ (centre) and Dy₂(Cnt)₃(thf)₂ (right).

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Emissive hybrid dynamers: Complementarities between cluster and supramolecular chemistries in the design of multifunctional materials

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Abstract

Stimuli responsive emissive materials have drawn an increasing attention for their potential in applications like sensors, lightning, optoelectronic or information storage. They are able to react to one or several external stimuli, such as a chemical or vapor exposure, a mechanical or electrical stress, a light irradiation, or a thermal treatment.^[1] Using supramolecular interactions to design stimuli responsive materials has a great potential in terms of reversibility of the material response.

The goal of this work is on one hand to design functional octahedral transition metal cluster hybrid compounds possessing self-assembling abilities and, on the other hand, to use these self-assembling abilities to make metal cluster compounds interact with organic chromophores in a new class of hybrid materials called «hybrid dynamers». To do so, we wish to couple octahedral clusters with organic luminophores using electrostatic interactions or complementary H-bond donor and acceptor moieties. The octahedral cluster complexes of transition metals of 6–7 groups (Mo, W, Tc, Re) are currently one of the most actively studied metal complex family due to their bright red-NIR luminescence,^[2] radiopacity,^[3] and reversible electrochemical transitions (in aqueous and non-aqueous solutions) in a narrow window of potentials accompanied by a significant change of their optical spectra.^[4] Up to now, metal cluster containing supramolecular materials involving H-bonds as the driving force to create the material have never been described. In this work we explored such innovative research field by designing specific organic and hybrid building blocks able to self-assemble in a controlled fashion leading to emissive materials with new properties. To do so, dynamers in which red-NIR emissive M₆ clusters were coupled to complementary organic emitters in a controlled and reversible way using supramolecular interactions, were investigated.

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ABSTRACTS OF POSTERS PRESENTATIONS

Study of the influence of atomization and functionalization treatment conditions on the microstructure of 316L(N) steel powder particles for consolidation by LPBF

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Abstract

Within the framework of the development of the additive manufacturing processes carried out by the CEA, this work aims at studying the influence of atomization and functionalization treatment conditions of grade 316L(N) steel powder particles, on the microstructure after consolidation by L-PBF. Previous work has demonstrated the impact of using different commercial 316L steel atomized powders on the microstructural characteristics of material obtained after consolidation by L-PBF process [1]. Especially, one of the tested powders led to the production of a material with a refined and quasi-equiaxial grain structure, unlike steels characterized by a columnar grain structure typically obtained by L-PBF with the same process parameters. Even if the mechanisms of this singular behavior are not clearly identified yet, the atomization conditions and the contents of minor elements and impurities in the powders seem to have a significant influence on the observed phenomenon. Indeed, TEM observations performed on the consolidated materials show that the refined microstructure has an enhanced precipitation density, due to fine chromium/iron carbides precipitates of around 20 nm diameter. These precipitates could act as additional nucleation sites, preventing the epitaxial growth of the grains during L-PBF consolidation. This specific precipitation, observed after L-PBF consolidation, is assumed to result from the atomization process conditions, inducing a low nitrogen content in powder particles.

This study aims at identifying the influence of the nitrogen content on the 316L steel consolidated by L-PBF microstructure. First, TEM observations have been performed to the specific 316L powder precursor, which show a fine precipitation currently under identification. Secondly, powders with various nitrogen levels are produced and studied. To control the nitrogen content of the powder, two processes are investigated: nitriding treatment of the reference powder, using nitrogen atmosphere, and ultrasonic atomization in controlled conditions. Afterwards, those powders are consolidated by L-PBF process with optimized and fixed parameters, in order to focus on the influence of the nitrogen content of the powder on the final microstructure. Finally, tensile tests/hardness tests are performed to compare the mechanical performances and identify the anisotropic behavior associated to each microstructure.

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Oxygen Reduction Reaction (ORR) electrocatalysis with functionalized plasmonic nanomaterials

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Abstract

Nowadays, developing “green” fuel cells is of paramount importance, where the activation of O_2 via electrochemical reduction is revealed to be a promising alternative to energy conversion technologies. Oxygen reduction reaction (ORR) plays a very important role in fuel cells and requires an efficient electrocatalyst that could undergo multielectron exchange processes. Au-based and Ag-based spherical nanoparticles functionalized through reductive grafting with calix[4]arene diazonium salts have been demonstrated to exhibit high catalytic performance and good durability compared to their citrate analogs.¹

This work explores the electrocatalytic properties of gold and silver anisotropic nanomaterials, that were synthesized via the seed-mediated growth method. Absorption properties of gold nanorods (AuNRs), gold nanobipyramids (AuNBPs), and silver nanostars (AgNSs) stabilized by CTAB, citrate, and calix[4]arene were measured via UV-visible absorption spectroscopy while their morphology and structure are examined via high-resolution transmission electron microscopy (HRTEM). We will study their electrocatalytic properties and compare their selectivity and efficiency toward ORR.

One further interest of these anisotropic nanomaterials is the variability of their plasmonic properties. They exhibit strong visible-spectrum absorption due to their localized surface plasmon resonances (LSPR) excitation (Figure 1). Electrocatalytic reactions could take benefit from plasmonic effects to boost performance.² Some preliminary results will be discussed.

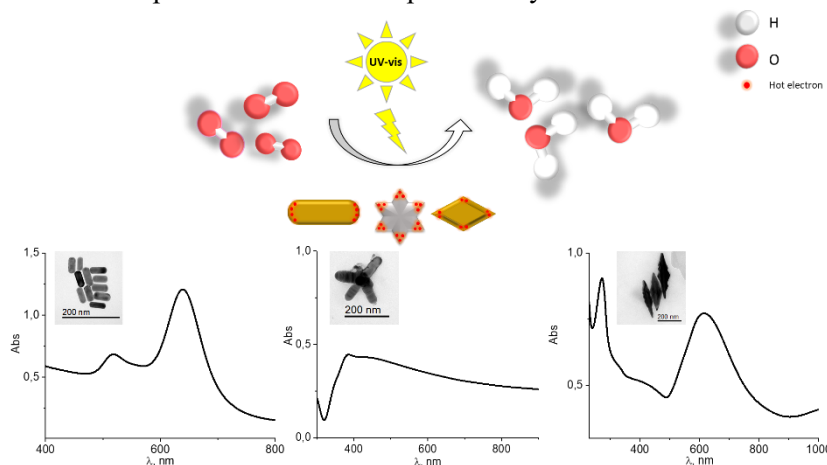


Figure 1. UV-Vis absorption spectra and TEM images of AuNRs, AgNSs, and AuNBPs.

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SLM 3D printed industrial electrodes for alkaline water splitting

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Abstract

The H₂ production from the electrocatalytic reduction of water or protons is currently arousing tremendous interest among the international community¹⁻³. Transition metals alloys are currently benchmarked to avoid using platinum as electrode material⁴. Selective Laser Melting (SLM) 3D printing is an emerging, powerful and few explored technique to fabricate transition metal alloys with unique geometries which could be used for efficiently producing H₂^{5,6}.

Our study aims to evaluate the interest of high surface area, alloyed and structured SLM 3D printed electrodes for the further industrial development of an alkaline water electrolyzer. We studied Ni-based transition metals binary alloys, with various shapes and surface morphologies, used both as electrolyzer anodes and cathodes. A deep understanding of these materials has been gained through the combination of multiple surface characterization techniques.

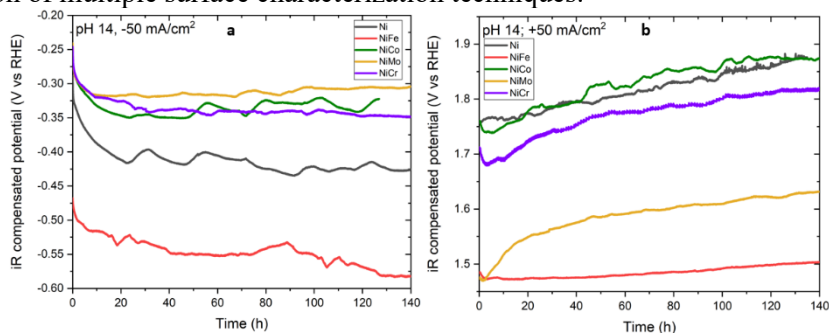


Figure 1. *iR*-compensated one-week chronopotentiograms at -50 mA/cm^2 (a) and $+50 \text{ mA/cm}^2$ (b) for five Ni-based materials in alkaline medium pH 14.

We have obtained reproducible values and consistent with past studies on metallic foils, and overpotentials lower than 0.3 V vs Reversible Hydrogen Electrode (RHE) at 50 mA/cm^2 . Compared to Ni, these are decreased by 0.1 V vs RHE for HER and 0.3 V vs RHE for OER at $\pm 50 \text{ mA/cm}^2$. Moreover, an outstanding stability is observed for all cathodes and some anodes.

Key words Water Splitting, Electrocatalysis, Alkaline Electrolysis, 3D Printing

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**Study of a new polymer matrix applied to the development of
printable magnetic composites**

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Abstract

The increase in the use of wireless technologies leads to a significant diversification of application contexts relative to electromagnetic waves emissions. Contextually, elaboration of innovative absorbent composite materials presents a great development potential of additive manufacturing techniques such as fused deposition modelling 3D printing.

The present study consists in elaborating composite materials filled with either lamellar or spherical ferromagnetic particles (Fe), aiming at designing a material, which is 3D printable and able to absorb electromagnetic waves.

All samples were prepared at molten state, from two references materials: on one hand, ABS/PE master batches prepared in an internal mixer with PE volume fractions from 10 to 40%, on the other hand, ABS/Fe composites elaborated using a twin-screw extruder at Fe volume fractions from 10 to 30%. Then, Fe particles were incorporated within either ABS neat matrix or ABS/PE masterbatch using twin screw extruder.

The linear viscoelastic measurements, at a temperature of 220°C used in both the elaboration process and 3D printing, highlight full thermal stability of all composites over 3,000 s, that is over the time needed for sample elaboration and 3D printing. The add of PE inclusions does not interfere on rheology and electromagnetic properties but leads to flow instabilities incompatible with fused deposition modelling 3D printing of ABS/PE/Fe samples.

A newtonian behavior of ABS/Fe composites is obtained with spherical Fe particles whereas a threshold behavior, attributed to lamellar Fe particles dispersion within ABS, is observed and does not contraindicate 3D printability: no clogging is observed through fine nozzles of 3D printing.

It is worth pointing out that electromagnetic properties of the materials are reproducible at different steps of the process, from extrusion to filaments elaboration and 3D printed samples. Surprisingly, a power law of relative viscosity versus magnetic loss is obtained with exponents strongly dependent of Fe particles aspect ratio; besides, composites with either 10% of Fe lamellar particles or 30% of Fe spherical particles have same rheology and also similar electromagnetic performances.

Freezing-enhanced zwitterion fluoroquinolones adsorption on goethite:
Contribution from ion pairing formation

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Abstract

The assessment of zwitterion fluoroquinolones (FQs) mobility in soil is of great interest due to their increasing threat to human health and ecosystem. Though it's well explored in various ambient systems, little is known about their adsorptive behaviors and binding mechanisms in frozen solutions. To address this issue, in this study we compared the adsorption of ciprofloxacin (CIP), a model zwitterion FQ, on goethite in ambient (25°C) and frozen solutions (-21°C) under different pH, electrolytes and ion strengths. A surface complexation modelling (SCM) was applied to predict pH-dependent adsorption of CIP in the aqueous solutions in the presence of three non-reactive anions: Cl⁻, Br⁻ and NO₃⁻. Anion type and concentration were found critical in controlling zwitterion FQs mobility by means of shielding effect. Anions ion pairing with CIP help minimize repulsive electrostatic interactions between CIP and charged surface, resulting in formation of ion-paired (IP) species of adsorbed CIP. Freezing, for the first time reported here, could induce greater adsorption at acidic pHs at lower ion strengths, by way of forming additional IP species of CIP. This could be ascribed to freeze concentration of anions, organic compounds, and iron oxides in the grain boundary region. *In situ* ATR-FTIR observation, combined with the SCM prediction, provided insightful evidences for the formation of additional CIP tridentate complexation onto goethite. These findings have strong implications in the prediction and development of new protocols for contaminant mobility and fate in icy environments in mid-latitude and mountainous regions

[PdHCu₁₁{S₂P(OⁱPr)₂}₆(C≡CPh)₄]
**a hydride-containing 2-electron superatom as electrocatalyst for
hydrogen production**

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Abstract

The recently characterized [PdHCu₁₁{S₂P(OⁱPr)₂}₆(C≡CPh)₄] nanocluster exhibits an unprecedented metallic core made of an incomplete Cu₁₁ cuboctahedron encapsulating a Pd atom at its center. The hydride ligand is coordinated from the inside, principally to Pd and more weakly to three Cu atoms. This cluster shows excellent electrocatalytic properties in the hydrogen evolution reaction (HER). Our calculations confirm the experimental position of the hydride and indicate that this cluster is a 2-electron superatom^[1-4] with 1S² 1P⁰ configuration, despite the presence of a vacant vertex on the copper icosahedron. The hydride makes a bond with the central Pd, in which a 4d(Pd) AO is involved. As a consequence, a PdH unit is created, which provides one electron to the [Cu₁₁]¹⁰⁺ polyhedron to complete the superatomic count. Thus, the presence of the hydride ensure stability to the incomplete cuboctahedron. This resulting incompleteness provides to the cluster with a void that calculations show to be a channel for an incoming hydrogen atom to access to the central Pd. This process constitutes the first step (Heyrowski step) of the HER catalytic cycle.

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Zr(IV) chelators for innovative diagnostic methods

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Abstract

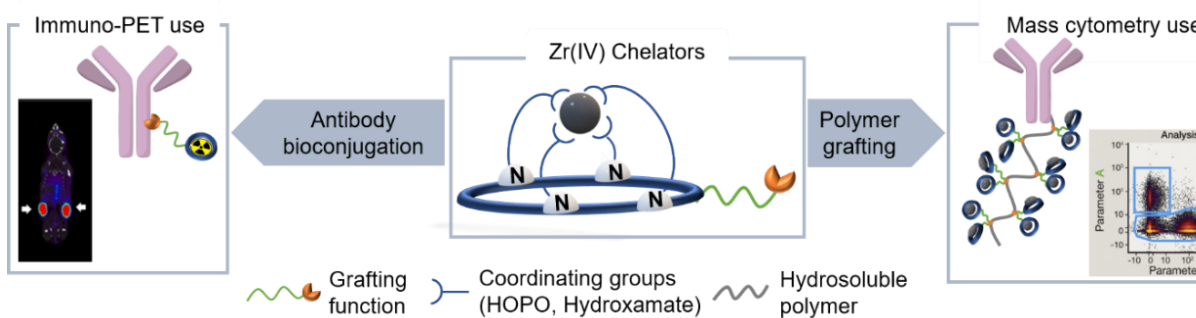
Keywords: PET-imaging; Mass cytometry; Cyclam; Zirconium; HOPO; Hydroxamate

Cancers and many serious diseases are becoming more and more complex to study through the years. It seems judicious to elucidate their origin, behavior and mechanism by combining anatomic scale diagnosis to monocellular scale analysis. This can allow earlier and more reliable diagnosis to improve and personalize the therapy.

PET-imaging is particularly sensitive imaging modality. Coupled to the specificity of an antibody, it leads to a targeted diagnosis called immuno-PET. Currently, ^{89}Zr ($t_{1/2} = 78.4$ h) is the subject of intense researches since it can be combined with antibodies with slow pharmacokinetic able to image tumors difficult to reach. However, the currently used ^{89}Zr chelator, deferioxamine B (DFO), has stability limits leading to ^{89}Zr release. The free radiometal therefore accumulates in bones and causes bones metastasis.^[1]

Mass cytometry (MC) is a powerful technique at a monocellular scale. The principle is similar to flow cytometry but the targeted cells parameters are detected by mass spectrometry. The unique properties of MC enable the identification of rare cellular populations, thanks to antibodies labelled by polymers functionalized by multiple copies of the same metal chelate.^[2] To prevent the cellular complexity, new metals such as Zr(IV) with its 4 stable isotopes are interesting. Actually, only one Zr(IV) containing polymer for MC has been synthesized. It uses DFO as Zr(IV) chelator but is limited by its low aqueous solubility.^[3]

The goal of this research is to develop new stable and inert Zr(IV) polyazamacrocyclic chelators functionalized with HOPO or hydroxamates coordinating groups, soluble in biological media and including a reactive chemical group. In this way, there will be usable for the conception of ^{89}Zr radiopharmaceuticals for immuno-PET or for the design of new Zr(IV) chelating polymers for mass cytometry.



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**^{29}Si and ^1H NMR structural study of chrysocolla, an amorphous copper containing silicate:
Application to archeological copper metallurgy**

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Abstract

At Ujina-Collahuasi (Tarapacá, Chile), an Inca camp of miners and more than 50 furnaces were discovered constituting the largest known pre-Hispanic copper production site for northern Chile^{1,2}. This unique archeologic site gives many clues to understand the functioning of the furnaces to reduce ores to metal. Among the copper ores used, there were malachite, brochantite, but also chrysocolla, an natural amorphous paramagnetic “mineraloid” with a proposed formula unit $\text{Cu}_2\text{H}(\text{Si}_2\text{O}_5)(\text{OH}) \cdot n\text{H}_2\text{O}$, which was always present in substantial proportion³.

A preliminary study showed that the slags contained a significant excess of silica, including some chemical phases rich in copper and silicon element. Concerning the origin of these phases, the principal hypothesis is the chrysocolla introduction and its important using. In order to understand how the metallurgical craftsmen of Collahuasi succeeded in reducing this copper ore into metal, we need a clear description of chrysocolla structure and its thermal degradation.

Farges *et al.*⁴ and, more recently, Stebbins⁵ had used with success XAFS and ^{29}Si solid-state NMR, respectively, to obtain structural information on the chrysocolla phase. But, amorphous and paramagnetic character of this natural compound make structural information uneasy to extract. In this work, we highlighted the **crucial importance of using adiabatic pulses to ensure a full excitation of the paramagnetic component**⁶ and to, thus, probe $^1\text{H} - ^{29}\text{Si}$ correlations. The results are completed by low temperature NMR experiments. In addition, in situ XRD analysis give some crucial informations on the thermal decomposition of Chrysocolla.

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Consideration of the electrokinetic leakage phenomenon for reliable electrokinetic characterization of polyelectrolyte membranes

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Abstract

The sensitivity of Zeta Potential (ZP) to the sign of the surface charge of membranes makes it interesting for the characterization of polyelectrolyte (PE) membranes. However, it has been shown that a parasitic phenomenon, the “electrokinetic leakage”, can lead to significant interpretation errors, especially for membranes having coarse-porous and/or hydrophilic supports [1,2]. This study demonstrates that applying the standard experimental protocols and Smoluchowski electrokinetic theory leads to inaccurate determination of the surface ZP of layer-by-layer (LbL) assembled polyelectrolyte membranes and even to potentially misleading conclusions about the sign of their surface charge.

We show how to take into account the electrokinetic leakage phenomenon and obtain a correct and accurate characterization of LbL membranes. The approach relies on the measurements of the streaming current between two membrane samples at different spacings. It allows an accurate determination of the surface ZP and provides information on the electrical charge of the sublayer(s) underneath the membrane skin layer.

Various flat-sheet membranes were modified using cationic (PEI, PAH) and anionic (PSS) polyelectrolytes. An example obtained with a coarse-porous membrane support is shown in Figure 1.

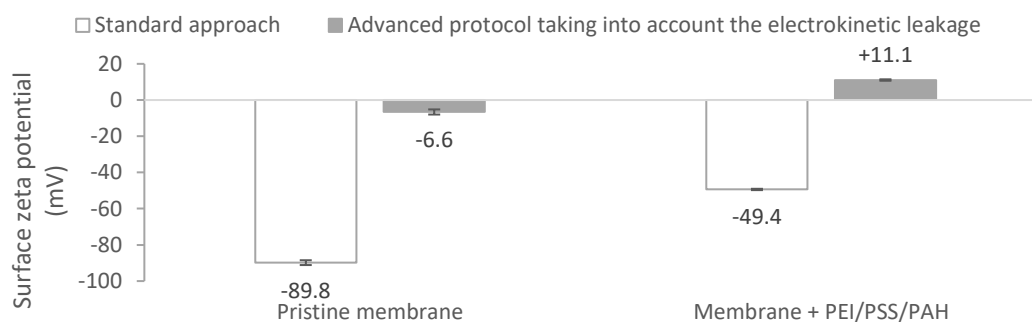


Figure 1 : Surface ZP of a coarse-porous membrane before and after PE deposition calculated with streaming current vs gap height measurements; measuring solution: 0.001 M KCl solution at pH 5.6 ±0.004.

Compared to a standard measurement protocol, taking into account the electrokinetic leakage into the membrane support leads to a pristine surface ZP correction of more than 90%. More strikingly, after LbL modification of the membrane terminated by a polycation (PAH) layer, the standard measurement protocol wrongly suggests a 45% ZP increase with no change of sign, whereas our advanced measurement protocol highlights the sign reversal of the surface charge due to polycation adsorption on the top surface. The consideration of the electrokinetic leakage phenomenon is thus essential for the reliable determination of the ZP of surface functionalized membranes.

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Design of core-shell particles for high-performance luminescent markers

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Abstract

Coordination polymers that contain lanthanide ions are already used in the industry as luminescent markers.¹ The point of using the core-shell architecture is to minimize the terbium-to-europium energy transfer that quenches the luminescence². The physical separation of both compounds in a core-shell organization has been observed and patented.³ It results in a significant increase of the luminance compared to a molecular alloy with identical composition.

To better understand the formation of core-shell particles, a fundamental study was performed on the solubility of compounds with general chemical formula $[Ln_2(bdc)_3(H_2O)_4]_\infty$ with Ln=La-Er plus Y and $bdc^{2-} = 1,4\text{-benzene-di-carboxylate}$.⁴ This investigation gave us insight into the thermodynamically favourable combinations for core-shell synthesis (Fig 1).

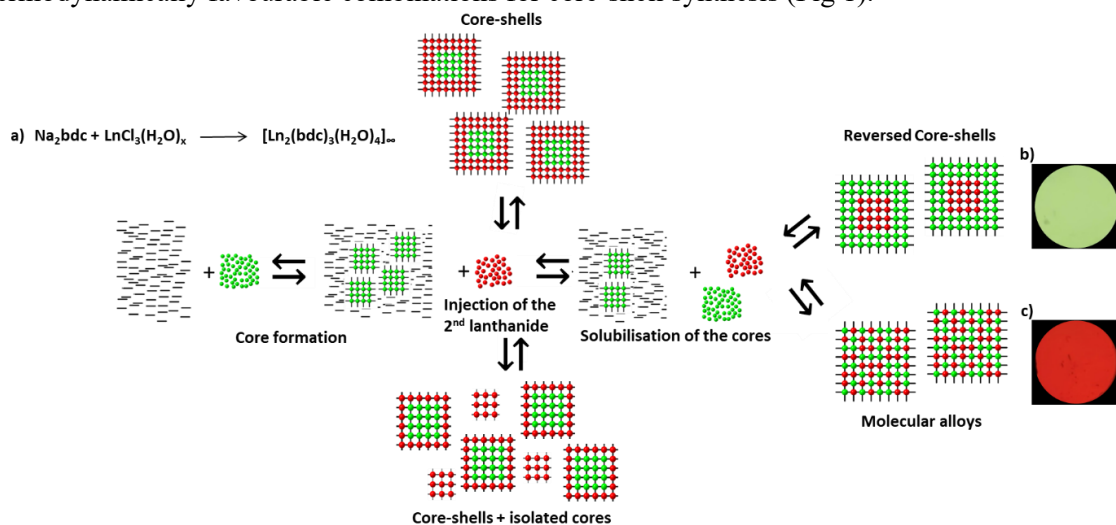


Fig. 1 : Depiction of the different plausible pathways during a core-shell microcrystalline powder synthesis; a) Chemical reaction leading to the formation of coordination polymers; b) and c) Pictures of $[Eu@Tb(bdc)_3(H_2O)_4]_\infty$ and of $[EuTb(bdc)_3(H_2O)_4]_\infty$ pellets, respectively, under UV excitation ($\lambda_{exc} = 312nm$).

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Chalcogenide glass shaped by additive manufacturing for IR optical applications

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Abstract:

Researches on additive manufacturing processes have considerably progressed in materials chemistry, especially for glasses with many methods currently used (SLM, SLA, FFF...). Chalcogenide glasses chemistry has also evolved and sectors are interested to produce optical devices in large quantities for imaging, sensors, optical fibers, etc. Lately, chalcogenide glasses such as As_2S_3 or $Te_{20}As_{30}Se_{50}$ were manufactured for the first time by 3D printing using FFF (Fused Filamentation Fabrication) process. In this context, Umicore IR Glass company is interested in this new chalcogenide glass shaping approach. The goal of this present study is to maintain IR transmission of the desired shape equivalent to melt quenched glass in 8-12 μ m window. In order to explore further the printability of various chalcogenide glasses, this study was conducted on the As_2Se_3 , a glass composition with higher thermal properties which has not been printed yet.

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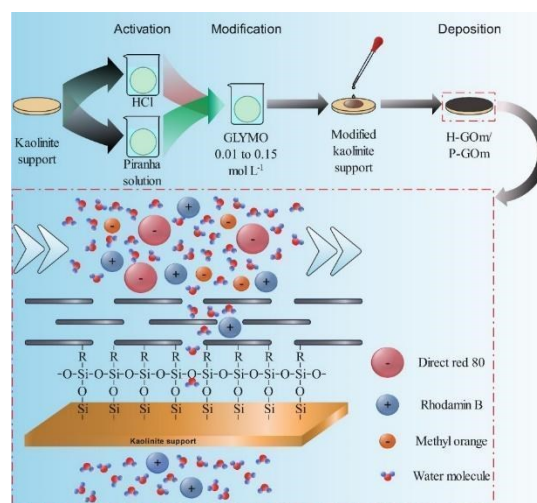
Enhancing Stability and Performance of Graphene Oxide Membranes Grafted on Low-Cost Rich-Silica Support: A Comparative Study of Two activation approaches

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Abstract

Although graphene oxide (GO) has shown encouraging results (high flux and rejections) in membrane field, it has a huge issue with stability when coated on ceramic supports, particularly those formed of geomaterials such as kaolinite. However, to prepare low-cost ceramic membranes using Moroccan geomaterials and use them as support for a GO stable layer is challenging.

This work aims at preparing stable GO layer deposited on a low-cost rich-silica support. The GO membrane was prepared using grafting approach, which included surface activation, then surface modification and a final coating (Figure 1). Silanol functions were activated using either piranha (hereafter denoted P) or HCl (hereafter denoted H) to determine which of them provided the highest membrane stability. Then the surface was grafted using 3-Glycidoxypropyltrimethoxysilan and according to FTIR, more GLYMO was grafted on membrane activated with piranha solution than with HCl. Finally, GO nanosheets were deposited using evaporation-assisted assembly leading either to P-GO membrane (P-GOM) or H-GO membrane (H-GOM). Stability test on the membrane demonstrated a highly stable GO deposited layer for P-GOM at different pH contrary to the non-grafted membrane and to H-GOM that peeled off from the support. For the P-GOM, the GLYMO concentration was investigated in the 0.01 to 0.15 mol L⁻¹ range and an optimal value of 0.05 mol L⁻¹ was evidenced. The deionised (DI) water permeance of the P-GOM was 5.61 L h⁻¹ m⁻² bar⁻¹ and the dye rejection at 3 bar for 50 ppm solutions was close to 90% for Direct Red 80 (MW = 1373.1 g mol⁻¹) and 81% for Rhodamin B (MW = 479 g mol⁻¹). The membrane fouling was partly irreversible as the DI water flux recovery was 80% after DI water rinsing.



Acknowledgment:

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The Natural Breakdown of Plastic Wastes and the Emergence of Resultant Products: An Experimental Study

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Abstract

Over the few last decades, global plastic pollution exponentially increased from 1.5 million tons to 359 million tons from 1950 to 2018 (PlasticsEurope, 2020), with 10 % of the produced waste expected to land as a destination in the ocean. Once released into the environment, plastic waste goes through multiple natural weathering processes, most likely mechanical abrasion, and photochemical oxidation (Andrady, 2011). These phenomena contribute to many changes in polymer properties: (i) chemical changes, (ii) physical changes (Anthony L. Andrady (2017)), (iii) generation of low molecule weight products (i.e. microplastics (MPs) and nanoplastics (NPs)), and (iv) release of additives (Charlotte Catrouillet et al., (2021)).

Often, UVB radiation in sunlight and oxygen are the primary factor in outdoor polymer weathering. According to the investigation by Rabiller-Baudry et al. (2020, 2021), it appears that polyethersulfone-based polymers can undergo accelerated degradation as a result of the combination of oxidizing agents and microwaves, resulting in degradation that has a similar effect to UV radical-induced photo-degradation. Adapting this methodology to polyethylene (PE) based plastics, an accelerated indoor aging experiment was carried out on formulated plastic samples, utilizing hydrogen peroxide and microwave irradiation.

In order to understand the physical and chemical changes induced by the aging protocol, and to characterize the resulting products (bulk plastics but also MPs and NPs) of the plastic alteration, a combination of qualitative and quantitative analysis was carried out. Techniques employed included SEM/TEM, A4F-UV-MALLS/NTA, TOC/ICP-MS, ATR-FTIR, and Pyro-GC-MS. Release patterns of inorganic additives from plastic matrices into the aqueous phase based on their nature (oxide nanoparticles or soluble elements) and their distribution within the plastic were obtained which will be discussed during the presentation.

**GOLD BASED ELECTROCHEMICAL APTASENSOR FOR
PHARMACEUTICAL POLLUTANTS RECOGNITION**

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Abstract

With the increased consumption, pharmaceuticals are ubiquitously present in the environment, causing hormonal disruption, a decline in animal populations, and contributing to the phenomenon of antibiotic resistance (1).

Their levels vary from $\mu\text{g/L}$ in wastewater to ng/L in river water, and traces in drinking water. A suitable analytical method requires a low limit of quantification, low cost, portability, and robustness. In this study, an electrochemical sensor capable of detecting erythromycin, a macrolide antibiotic pollutant was developed.

Three gold platforms were tested, a commercially available gold nanoparticles screen-printed electrode and two platforms generated by grafting the gold nanoparticles from a HAuCl_4 solution on a carbon screen-printed electrode by cyclic voltammetry and chronoamperometry. On the optimized gold platform, the thiolated aptamer that gives the specificity of the method was immobilized by multipulse amperometry. The next step was the immobilization of 6-mercapto-hexanol (MCH) to occupy the free gold sites and to ensure a good spatial organization of the aptamers. The obtained aptasensor was incubated at room temperature with the analyte and the signal was registered (Figure 1).

Each step was characterized by differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) using a ferrocyanide/ferricyanide couple as a redox probe. The aptamer immobilization and MCH blocking were emphasized by the electrode passivation, while the incubation with erythromycin resulted in further passivation due to the aptamer folding upon binding. The signal generated by the erythromycin permitted the detection of the molecule until concentrations of $1 \mu\text{M}$. The designed aptasensor fulfills the desired sensitivity through the gold nanoparticles, the selectivity through the aptamers, the portability with the screen-printed electrodes, and the low cost, being an optimal tool to monitor the water quality.

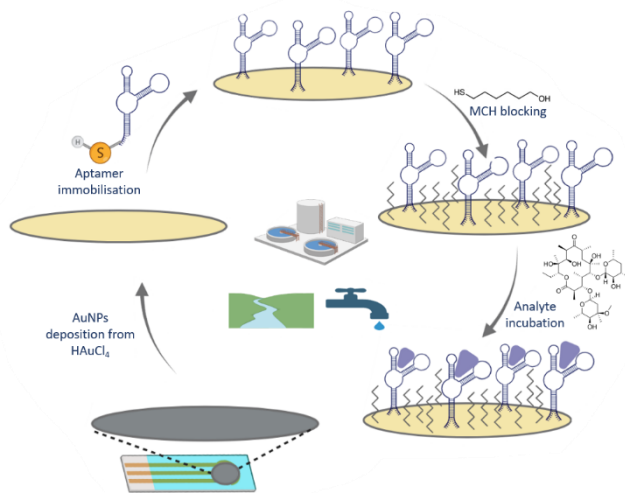


Figure 1. Schematic representation of the electrochemical aptasensor development for

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**Facile MOF Support Improvement in Synergy with Light
Acceleration for Efficient Nanoalloy-Catalyzed H₂ Production from
Formic Acid**

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Abstract

Hydrogen (H₂) generation and storage are actively investigated to provide a green source of energy, and formic acid (HCOOH), a major product from the biomass, is regarded as a productive source of H₂. Therefore, improvements in heterogeneous catalysts are called for. Here, a novel type of catalyst support is proposed involving simple addition of the mixture of metal ion precursors to core-shell ZIF-8@ZIF-67 followed by reduction with NaBH₄, with performances surpassing those obtained using nanocatalysts in ZIF-8 or ZIF-67. The nanocatalysts Pd₂Ag were optimized with ZIF-8@Pd₂Ag@ZIF-67 under visible light illumination for selective HCOOH dehydrogenation involving turnover frequency (TOF) value of 430 h⁻¹ under light irradiation at 353 K. These results also reveal the crucial roles of the Pd sites electronically promoted in the presence of visible light by the Ag plasmon resonance and the advantageous core-shell MOF structure. In order to examine the potential extension of this catalyst improvement principle to other catalytic reactions, 4-nitrophenol reduction, a benchmarking model of catalytic reaction, was tested, and the results also confirmed the large performance superiority of ZIF-8@Pd₂Ag@ZIF-67 over Pd₂Ag@ZIF-8 and Pd₂Ag@ZIF-67, confirming the interest of the novel catalyst design.

ANALYTES DETECTION BY LUMINESCENT Ln MOFs: FIRST TRIALS USING Tb AND Eu OH-BENZENEDICARBOXYLATES

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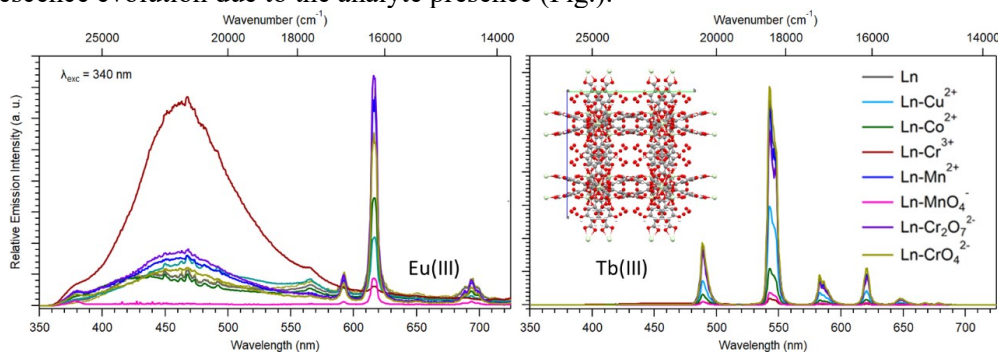
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Abstract

Metal-Organic-Frameworks (MOFs) are porous coordination polymers that have been studied for the past twenty years due to the multiplicity of their crystal structures and their various possible applications (molecules storage/separation, catalysis...). Such diversity comes from the MOFs' building units: organic ligands associated with metallic cations or polynuclear centers. Lanthanide ions possess high coordination degree (7-12) which confers high stability of the resulting MOF. Furthermore, lanthanides have numerous very thin emission bands allowing their signature in luminescence measurements. In particular, Eu^{3+} and Tb^{3+} are emitting in the red and the green domain, respectively. Combining one of these lanthanide ions with a chosen ligand, one may be able to trap analytes inside the MOF framework and to obtain a quick luminescent response hence forming a chemical sensor.

In this work, the focus has been directed on MOFs using Tb^{3+} or Eu^{3+} ions with 2-hydroxy-1,4-benzenedicarboxylic acid (OH-H₂BDC) previously studied in our group^[1] and particularly in one structure, obtained for homo-nuclear lanthanides (La-Nd). The MOFs crystalize in the cubic system with large square section channels (11x11 Å, Fig.) that contain the crystallization water molecules. The driven idea was to synthesize MOFs possessing this structure with Eu^{3+} and Tb^{3+} and to use the channels and the hydroxy functions to trap analytes in solutions and then to study the luminescence response of these materials. MOFs have been successfully synthesized for Eu/La and Tb/La mixtures. Also, the stability of these MOFs has been studied (pH, temperature, solvents) then followed by reactions in solutions containing various analytes (transition metals cations) to finally assess the luminescence evolution due to the analyte presence (Fig.).



Solid-state visible emission spectra at room temperature of (left) Eu_{80}La MOF vs Eu_{80}La + analytes, (right) Tb_{80}La MOF vs Tb_{80}La + analytes) and projection along the a-axis of the crystal structure of $[\text{Tb}_{0.8}\text{La}_{0.2}(\text{OH-HBDC})(\text{OH-BDC})\cdot 9\text{H}_2\text{O}]_{\infty}$

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**Cooperative Spin crossover Behaviour in Binuclear Fe(II) Complex
Based on Functionalised Triazole ligand**

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Abstract

Spin crossover (SCO) complexes constitute one of the most spectacular examples of molecular bistability. The spin crossover phenomenon is known since the early 1930s^[1] and has since then attracted a lot of interest related to the SCO characteristics of the material such as the cooperativity, since the presence of hysteretic effects originate potential applications such as data storage and displays.^[2-4] Cooperativity which usually accompanied by hysteretic behaviour is the only fundamental property since the change of colour and volume occurring during the transition could be of particular importance for development molecular devices, such as sensors.^[5]

Here we present, a new iron(II) binuclear complex of formula $[\text{Fe}_2(\text{C}_9\text{H}_{11}\text{-trz})_2(\text{tcm})_2]$ ($\text{C}_9\text{H}_{11}\text{-trz}$ = 4-Cyclopentyl-4H-[1,2,4]triazole, tcm = tricyanomethanide), characterized by single crystal X-ray diffraction, DSC and magnetic measurements. The magnetic and DSC studies show an abrupt High Spin (HS) \leftrightarrow Low Spin (LS) transition with a hysteresis loop of 10 K ($T_{1/2} \approx 201 \downarrow \text{K}$; $T_{1/2} \approx 210 \uparrow \text{K}$).

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**Thermodynamic calculations and experimental results of a
bioinspired mixture from lichens: [Malic acid][Glutamic acid], a
new deep eutectic solvent?**

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Abstract

Lichen is a pioneer species capable of surviving harsh environmental conditions such as hydric stress or high temperatures¹. We assume that in order to survive, the lichen holds a non-aqueous liquid system in its physiological environment². Based on these unique characteristics, we seek to develop these systems, named deep eutectic solvents (DES). Resulting from the association of a donor(s) and an acceptor(s) of hydrogen bonds, they are a new generation of greener solvents due to their properties (non-volatile, low toxicity and good solvation and extraction properties)³.

In this study, we used lichenic metabolite scaffolds from several selected lichen species (*Pseudevernia furfuracea*, *Evernia prunastri*, *Cladonia furcata* and *Lichina pygmaea*) as source of bio-inspiration for our formulations of new natural deep eutectic solvents (NaDES)⁴. To facilitate the choice of the syntheses to be carried out, we use prediction tools, such as COSMO-RS (COnductor like Screening MOdel-Real Solvents).

Among the prediction calculations performed, the association [Malic acid][Glutamic acid] seemed the most interesting. Nevertheless, we realized that depending on the involvement or not of zwitterionic forms in the calculations, the association of these two molecules is less promising. We therefore tried to reproduce these mixtures in the laboratory; it appeared that in order to obtain a homogeneous liquid, it is necessary to heat the mixture at high temperature. Moreover, we observed that a part of the glutamic acid cyclizes into pyroglutamic acid, giving rise to a ternary DES⁵.

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**Formulation of enzymatic detergents for the cleaning of
ultrafiltration membranes fouled by skim milk**

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Abstract

PES/PVP membranes are widely used for skim milk ultrafiltration. Membranes are systematically fouled by proteins which can only be removed by cleaning. Enzymes are eco-friendly. However, used alone, they are generally not efficient enough. So, to increase their efficiency, formulated enzymatic detergents must be developed. The formulated detergent may be decomposed in an enzyme, a buffer and a matrix containing all other ingredients. It can be challenging to master all the impacts associated with the choice of enzymes as only stabilized enzymes are commercially available. The stabilizing agents could potentially have an impact on the final detergents' performances due to interactions with the matrix ingredients. To account for the impact of these stabilizing agents, a prototype matrix has been formulated by our industrial partner (Hypred®, France) in which one among 3 different stabilized subtilisins (classical proteases used for membrane cleaning) has been dissolved (same hydrolysis activity). Only part of the stabilizers was identified thanks to the safety data sheets given by the enzyme providers. The selected UF membrane (HFK-131, Koch) has been fouled by skim milk in standardized conditions (50°C, 2 bar, 0.5 m. s⁻¹, 180 min). Then, the cleaning efficiency of the prototype detergents was evaluated at 50°C (2 bar, 0.5 m. s⁻¹, 60 min) by the mean of the residual protein quantification on membrane (ATR-FTIR). All detergents were very efficient. As general trends, the water flux recovery (WFR) was high but sometimes greater than 100%. A de-formulation approach was undertaken aiming at understanding the origin of this behavior. Based on complementary ATR-FTIR characterization of membranes at every step, the discussion aims at providing a fundamental explanation of the WFR behavior, not systematically associated with membrane degradation. The respective role of stabilizers and matrix ingredients provide keys to go ahead in the formulation optimization.

**Synthesis and evaluation of improved glycogen synthase kinase
GSK-3 α inhibitors in glioblastoma cells**

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Abstract

The challenge for the design of glycogen synthase kinase-3 (GSK-3) inhibitors lies in achieving high selectivity for one isoform over the other. The therapy of certain cancer diseases, such as glioblastoma, may require specific targeting of the α -isoform⁽¹⁾. Here we report the design, synthesis, and evaluation of a novel series of inhibitors of the α -isoform of GSK-3. The starting point of these studies was CD-07⁽²⁾, a selective inhibitor previously identified in the group (with IC₅₀ of 4.8 nM and 22 nM against GSK-3 α and GSK-3 β , respectively). By taking into account structural modifications from molecular modeling, we prepared derivatives of the oxazolo[5,4-*f*]quinoxaline heterocycle that were evaluated for their activity on a panel of protein kinases. At the end of this study, the compound MH-124 proved to be the most potent and the most selective for the α isoform. Indeed, IC₅₀ values of 17 nM and 239 nM were determined against GSK-3 α and -3 β , respectively, showing almost fourteen times stronger selectivity for the α isoform. Finally, the efficacy of MH-124 was evaluated on two glioblastoma cell lines. Although MH-124 alone did not have a significant impact on cell survival, its addition to temozolomide (TMZ) significantly reduced the IC₅₀ value of the latter on the cells tested.

Film formation kinetics of rubber particles from *Hevea* latex in their hydrated state at the air-liquid interface

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Abstract

The latex exuding from the bark of *Hevea brasiliensis* tree after tapping is a colloidal suspension of various micrometric objects, mainly composed of rubber particles (RP) which contain cis-1,4-polyisoprene chains. *Hevea* latex is the only commercial source of natural rubber (NR), a strategic raw material used for automotive, medical and consumer applications. It is interesting to note that RP exhibit a bimodal size distribution with the presence of small rubber particles (SRP, diameter ~ 0.05-0.4 μm) and large rubber particles (LRP, diameter ~ 0.4-3.0 μm). The hydrophobic cis-1,4-polyisoprene core of RP is surrounded by a lipoprotein monolayer membrane. This biochemical composition vary according to their size [1]. The size of ammonia-stabilized RP has also been shown to influence various properties of NR samples. For example, the size of the RP impacts the formation of RP films, as well as the mechanical properties of NR [2]. However, drying of the film leads to rearrangement and deformation of the particles.

In this study, we propose a new approach where RP are characterized in their hydrated state by forming RP thin films at the air-liquid interface. In this way, they remain as close as possible in their native state, *i.e.* when the latex exudes from the tree. The adsorption kinetics of the ammonia-free RP is monitored by surface pressure and ellipsometric angle measurements, and completed by a visualization of the film by atomic force microscopy (AFM). The results show an influence of the particle size (SRP and LRP) on the interfacial behavior and on the film formation kinetics. This work provides a new insight into the behavior of hydrated ammonia-free RP films.

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Effect of DNA's molecular weight on its rheological behavior and flow birefringence appearance

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Abstract

Nucleic acids are natural biomacromolecules that are classified into deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), which are present in all living organisms, where they play fundamental roles in many biological processes.¹ The study of the dynamics of nucleic acids in solution, their flow properties and viscoelasticity is of great importance for understanding their biological functions.² Many important properties of nucleic acids, such as DNA, depend on polymer concentration, C_{DNA} , molecular weight (M_w), rigidity and external salt content, the latter parameter affecting electrostatic interactions.^{3,4} Furthermore, DNA molecular chains can organize, *in vitro*, into liquid crystalline phases at high C_{DNA} .

In this work, three DNA samples with different M_w were studied in solution in a broad concentration range (C_{DNA} from 0.025 to 200 mg/mL, depending on DNA M_w). Firstly, the intrinsic viscosities and M_w for all DNA samples were determined through capillary and rheological measurements. Then, the overlap concentrations, C^* , were estimated from the relation $C^* \sim [\eta]^{-1}$. DNA chain characteristics were then analyzed in terms of the influence of DNA M_w on the solution viscosities and on the overlap parameter, $C_{DNA} [\eta]$. Flow birefringence appearance was identified by screening a wide C_{DNA} range through visual observations with crossed polarizers. Crossed-light polarized microscopy was used to identify the appearance of liquid crystals at rest, confirming that higher C_{DNA} are needed to obtain liquid crystals for low M_w DNA samples. With the obtained information, the rheological behavior of selected DNA samples in the semi-dilute regime without entanglements (between C^* and C^{**}) and in the entangled regime ($C_{DNA} > C^{**}$) was studied through dynamic, flow and transient measurements. It was found that as the M_w of DNA decreases, more concentrated solutions are required for the appearance of flow birefringence, as well as for the formation of liquid crystals at rest.

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The excitation of ethynyl in the interstellar medium : A key to understand isotopic fractionation ?

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Abstract

Since the discovery of the ethynyl CCH radical in the interstellar medium, it has been detected in a wide range of astrophysical environments. It is one of the most abundant hydrocarbon in space and together with its detected isotopologues (CCD, ¹³CCH and C¹³CH), they are useful tracers of physical conditions. Indeed, as abundances strongly depend on the formation pathways, the measurement for the ratio [CCD]/[CCH] may constrain the age of molecular clouds in astrophysical models. However, hyperfine resolved ¹³C-based spectra show a higher intensity in favor of C¹³CH lines than ¹³CCH ones whereas their formation path is supposed to be the same. It is then of high interest to investigate this apparent different abundance of the two isotopologues.

An accurate interpretation of these observations requires to determine precise rate coefficients. Such quantities are necessary for non local thermodynamic equilibrium modeling which takes into account competition between radiative and collisional processes.

Non zero nuclear spins from ¹³C, D and H atoms lead to a resolved hyperfine structure for these species. Such complex energetic structure is a real theoretical challenge as exact scattering calculations are not feasible in a reasonable time. Then, it is necessary to develop numerical and methodological tools in order to determine accurate collisional data for astrophysical applications. In this poster, I will present the calculations of new accurate collisional data for all the CCH isotopologues.

Scattering calculations have been performed using a recoupling technique in order to determine accurate hyperfine resolved rate coefficients of CCH and its isotopologues in collision with H₂. These data were derived for a large range of temperature and are expected to improve abundance ratio calculations and better understand the evolution of the isotopic fraction in astrochemical models.

Multi-ion physical modeling of nanofiltration/low-pressure reverse osmosis with and without ozonation pretreatment

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Abstract

Since the last decades, an increase of numerous substances including organic matter and emerging micropollutants (MPs) which may affect human and animal health has been observed in aquatic environments 1. Conventional treatments of this increasing organic matter, for drinking water production, require increasing doses of coagulation and flocculation chemicals and generate increasing sludge production. Their limited effectiveness may increase the residual organic matter in the treated water and the risk of formation of disinfection by-products. Nanofiltration (NF) or low-pressure reverse osmosis (LPRO), integrated in more sustainable treatment lines, are proven to improve the treated water quality and contribute to retain MPs, while limiting sludge production and chemical consumption. Nevertheless, organic fouling is one of the main issues related with membrane processes. The potential benefits of pre-ozonation upstream membrane processes are investigated in the context of various drinking water production treatment lines. Thus, firstly, the transport properties of NF membranes are studied by means of the SEDE (steric, electric, and dielectric exclusion) homogeneous model. Within this 1D-model, the separation of solutes is considered as resulting from transport effects (described using extended Nernst-Planck equations) and interfacial phenomena, including steric hindrance, the Donnan effect, and dielectric exclusion in terms of both Born dielectric effect and image force contribution 2. Secondly, a pre-ozonation upstream of a NF membrane was investigated, as part of the development of a new treatment line of water loaded with natural organic matter, to potentially reduce the organic fouling and consequently to increase the permeate flow rate and/or to limit the concentrate volume 3 and to potentially improve the removal efficiency of MPs of interest, targeting modifying their ionic properties, without degrading the organic matter or MPs into by-products likely to degrade the quality of the filtered water. Meanwhile, based on the results obtained in the pre-ozonation study, the SEDE model is evaluated to verify the description ability for the complex water matrix containing micropollutants. It is noticed that the pre-ozonation has a minor impact on studied MPs rejection by the NF membrane. However, it is found that a relatively low specific ozone dose could effectively reduce the hydrophobicity of organic matter according to the fluorescence results which could potentially be a useful indicator for studying the impact of pre-ozonation on fouling mitigation. With respect to modeling, it is shown that the SEDE model can provide trends, however with significant differences between the MPs rejections simulated by the model and the rejection obtained experimentally. Therefore, improvement of the model should be considered for predictive purposes. Moreover, the same methodology will be conducted with the LPRO membrane to compare with the results previously mentioned of NF membrane regarding the objectives.

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Synthesis and reactivity studies of bioactive glasses, contribution to the preparation of 3D structures by additive synthesis

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Abstract

Biomaterials represent a major therapeutic challenge for the upcoming century in an increasingly ageing population where trauma or bone loss is not uncommon. Among these biomaterials are bioactive materials, including bioactive glasses(1), which generate a series of physicochemical reactions at the tissue/glass interface. The trend in recent years has been towards tissue engineering, and more particularly computer-assisted tissue engineering using these biomaterials(2), a practice that is growing in the medical field and is increasingly used in therapeutic procedures for bone reconstruction(3). To do so, supports (also called scaffolds) are designed, using 3D printing, most often using biocompatible polymers coupled with mineral fillers such as bioglasses.

Among the biopolymers available in the world, polylactic acid (PLA) is one of the highest biopolymers produced globally(4). This is partly due to its reliable cost and high abundance, but also to the fact that it has the advantage of being biocompatible and degradable in human body fluids and it can be assembled with other biocompatible materials such as bioactive glasses(5). We used the Fused Filament Fabrication using the Ender 3 Pro printer to design composite scaffolds using polylactic acid as the polymer and bioactive glass(6,7).

This poster presents the results of the study of the impact of the manufacturing parameters (pressure, shaping, mineral load, etc.) as well as the physicochemical and biological characterizations carried out on the scaffolds(8).

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Mots-Clés: scaffolds, bioactive glasses, PLA, bioprinting, tissue engineering

PICOSECOND ACOUSTICS AND FEMTOMAGNETISM

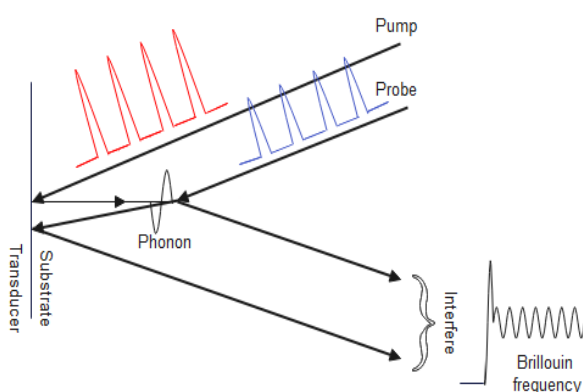
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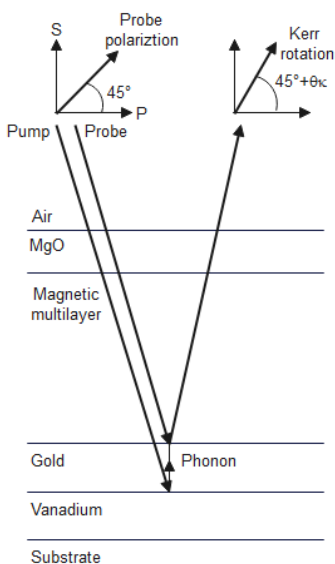
Abstract

The development and optimization of tools and investigation technics is crucial for the understanding of material properties. In this presentation, we will show some examples using picosecond acoustics for the measurement of some samples mechanical properties, femtomagnetism for the measurement of magnetism at femtosecond timescale, and some results merging both techniques for the investigation of the interplay between mechanics and magnetism.



Picosecond acoustics is an efficient technique for the investigation of mechanical properties at the micro- to nano- scale. To perform such measurements, we use a full optical pump-probe setup. A femtosecond pump pulse induces thermal expansion in a metallic transducer that generates acoustic waves in the investigated medium. The launched acoustic phonons are optically probed from photon-phonon interaction processes that allows the determination of the phonon velocity and material properties such as photo-elastic coefficients and components of the Hooke

tensor.



This femtosecond pump-probe setup allows as well the investigation of the magnetic properties of magnetic materials. To investigate at ultrafast timescale the magnetic properties (saturation, remanence, coercive field and magnetic anisotropy coefficient) of a magnetic sample, we perform femtosecond magneto-optical Kerr effect (rotation of the light polarization proportional to the magnetization) experiments. The femtosecond laser pump pulse has the ability to demagnetize magnetic materials at a femtosecond timescale. The femtosecond probe allows the observation of demagnetization, remagnetization and acoustic perturbation of the magnetization induced by the laser pump. During the remagnetization process, we can also observe Larmor precession of the magnetization (this will be useful for future improvements). The introduced methods are based on non-resonant excitation and are necessary to prepare future resonant measurements that are expected to provide a better signal to noise ratio and most importantly to induce magnetization reversal.

Fatigue life reinforcement of natural rubber: effect of torsion loading

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Abstract

Carbon Black filled Natural Rubber (CB-NR) is the most commonly used crystallizable elastomer for antivibratory applications. CB-NR exhibits a lifetime reinforcement in uniaxial fatigue when it is submitted to a non-relaxing loading (strictly positive minimum load). Since the lifetime reinforcement has not been observed or to a lesser extent for non-crystallizable rubbers, strain-induced crystallization (SIC) is generally considered to be responsible for this reinforcement. Nevertheless, this reinforcement and its intensity under other types of loading have rarely been investigated. In the late 2000s, special attention was paid to multiaxial fatigue in order to better meet the needs of industrial applications. However, the applied loads were mainly relaxing, which is not always the case in many applications. The present work aims at investigating the effect of non-relaxing torsion loadings on the fatigue lifetime reinforcement of CB-NR. For that purpose, pure torsion fatigue tests with different loading ratios have been performed with axisymmetric-shaped specimens at 23°C. The finite element method is used to predict the mechanical response at any point in the specimens. The prediction is significantly improved by taking into account the heterogeneous accommodation. First, it has been shown that non-relaxing torsion induces strong lifetime reinforcement. Second, the post-mortem analysis performed at the macroscopic and microscopic scales allowed us to identify the damage mechanisms, especially in the cases where reinforcement has been observed. At the microscopic scale, fatigue striations attributed to SIC were observed under non-relaxing torsion. The role of SIC in the damage mechanisms under torsion loading has been determined and linked to the loading conditions by using a pseudo-Haigh diagram.

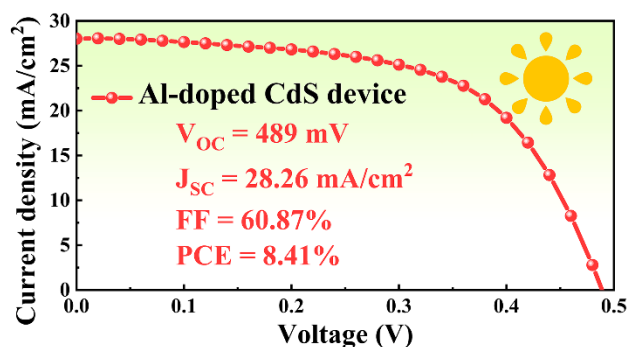
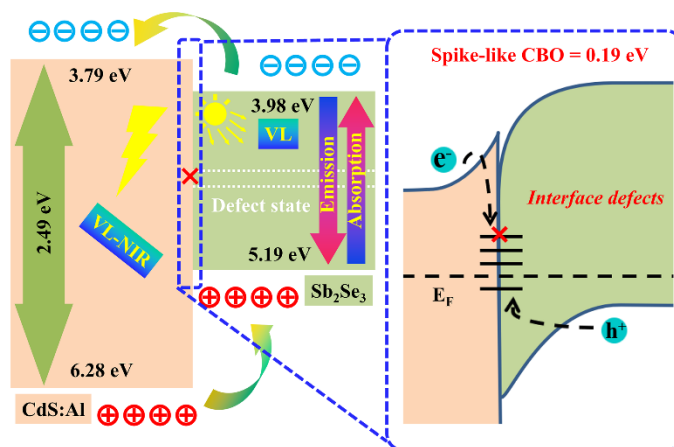
Carrier Transport Enhancement Mechanism in Highly Efficient Antimony Selenide Thin-Film Solar Cell

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Abstract

Exhibiting outstanding optoelectronic properties, antimony selenide (Sb_2Se_3) has attracted considerable interest and has been developed as a light absorber layer for thin-film solar cells over the decade. However, current state-of-the-art Sb_2Se_3 devices suffer from unsatisfactory “cliff-like” band alignment and severe interface recombination loss, which deteriorates device performance. In this work, the heterojunction interface of a Sb_2Se_3 solar cell is improved by introducing effective aluminum (Al^{3+}) cation into the CdS buffer layer. Then, the energy band alignment of $\text{Sb}_2\text{Se}_3/\text{CdS}:\text{Al}$ heterojunction is modified from a “cliff-like” structure to a “spike-like” structure. Finally, heterojunction interface engineering suppresses recombination losses and strengthens carrier transport, resulting in a high efficiency of 8.41% for the substrate-structured Sb_2Se_3 solar cell. This work proposes a facile strategy for interfacial treatment and elucidates the related carrier transport enhancement mechanism, paving a bright avenue to overcome the efficiency bottleneck of Sb_2Se_3 thin-film solar cells.



Over 12% efficient kesterite solar cell via back interface engineering

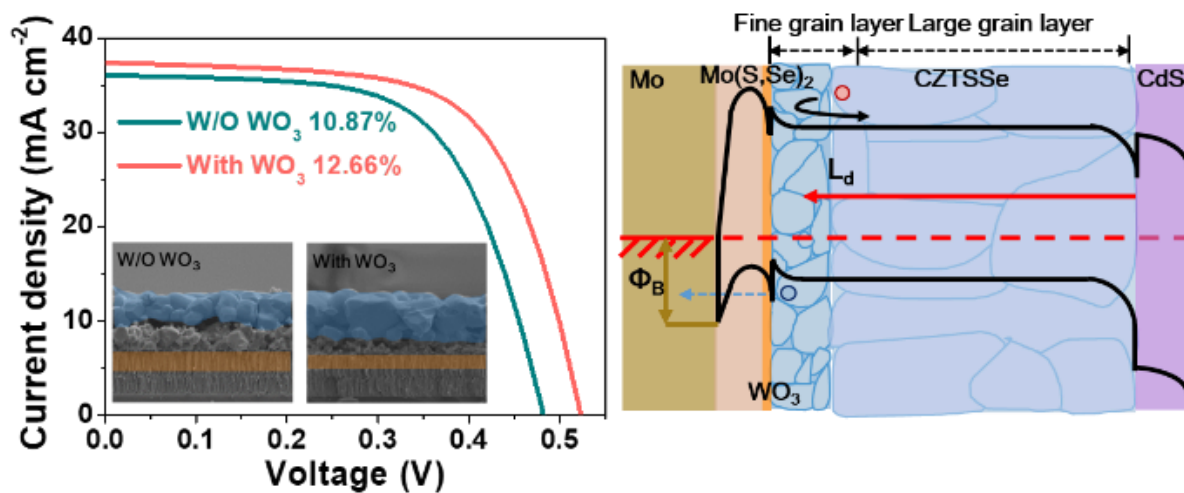
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Abstract

Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has attracted considerable attention as a non-toxic and earth-abundant solar cell material. During selenization of CZTSSe film at high temperature, the reaction between CZTSSe and Mo is one of the main reasons that result in unfavorable absorber and interface quality, which leads to large open circuit voltage deficit ($V_{OC}\text{-def}$) and low fill factor (FF). Herein, a WO_3 intermediate layer introduced at the back interface can effectually inhibit the unfavorable interface reaction between absorber and back electrode in the preliminary selenization progress; thus high-quality crystals are obtained. Through this back interface engineering, the traditional problems of phase segregation, voids in the absorber and over thick $\text{Mo}(\text{S},\text{Se})_2$ at the back interface can be well solved, which greatly lessens the recombination in the bulk and at the interface. The increased minority carrier diffusion length, decreased barrier height at back interface contact and reduced deep acceptor defects give rise to systematic improvement in V_{OC} and FF, finally a 12.66% conversion efficiency for CZTSSe solar cell has been achieved. This work provides a simple way to fabricate highly efficient solar cells and promotes a deeper understanding of the function of intermediate layer at back interface in kesterite-based solar cells.



IN SITU DIFFRACTION STUDY OF THE PHASE
TRANSFORMATIONS OCCURRING IN THE
THERMOELECTRIC COLUSITE $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$

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Abstract

Interest in thermoelectric (TE) technology has been continuously growing in the last decade driven to the necessity to limiting waste heat during energy transformation. Among the most promising TE materials at medium temperature, complex copper-based sulphides are of double interests as they are usually made of eco-friendly and low cost elements¹ and exhibit intrinsically low thermal conductivity.^{2,3} Derivatives of the natural mineral colusite, with general formula $\text{Cu}_{26}\text{A}_2\text{E}_6\text{S}_{32}$, (A = V, Nb, Ta, Cr, Mo, W; E = Ge, Sn, As, Sb), are an emerging class of excellent thermoelectric materials.⁴ As example, the ZT value of the $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$ rises to near unity at 675K, making this material one of the best p-type TE in this temperature region.⁵ Its performances are mainly related to the coexistence of an ordered (*P-43n*) and a disordered (*F-43m*) forms obtained after sintering at 1023 K (i.e. sample H), leading to a very low thermal conductivity.^{5,6} In addition, colusite is known to exhibit an intrinsic exsolution phenomenon supposed to be related to the coexistence of Sn-rich and Sn-poor colusites.^{7,8} In this study, we investigated by *in-situ* synchrotron powder diffraction the solid-state phase equilibrium as function of the temperature between the ordered and disordered forms of colusite $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$. The use of high-resolution setup revealed a complex behavior with several phase transformations, probably related to a mutual interaction and kinetic effects.

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New chiral conjugated polymers based on a helicene moiety for increased performances in optoelectronic applications

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Abstract

Conjugated polymers (CPs) provide unique synthetic challenges to tailor their chemical, electronic, and processing properties while identifying significant structure-to-property correlations. Over the past half-century, chemists have worked towards synthesizing more complex and solution processable conjugated polymers while approaching structural perfection. These efforts aim to maximize their beneficial properties such as high charge mobilities, impressive absorption and emission signals, as well as the ability to stabilize charges, among others. In this context, new synthetic approaches such as the use of chirality continue to elevate the field of conjugated polymers.¹ That's why helicenes,² fully π -conjugated helical molecules that possess fascinating chiroptical properties, can represent an obvious choice as building blocks to be utilized and synthesize unprecedented chiral conjugated polymers.

In this work, we present a range of new chiral conjugated polymers based on a helicene moiety coupled with the well-studied IndacenoDiThiophene (IDT). These wide bandgap, helicene-based polymers were for the first time integrated and thoroughly characterised into optoelectronic devices, more specifically OPVs. There, we managed to tackle to a certain extent both the small-scale, the low solubility, the reactivity and the processability issues often encountered on that kind of molecule. Following the robust conditions of Stille coupling, several statistical chiral CPs were synthesized. Racemic mixtures and several other homopolymers were also synthesized for comparison purposes as well as probing the effect of the orbital energy levels in the device. They were then extensively characterized to draw several interesting trends on the effect of the helicene moiety on the polymer's properties. Finally, OPVs were fabricated for most of the compositions, allowing us to show the superior device performances of the chiral polymers over their racemic counterparts. We there demonstrate a Power Conversion Efficiency (PCE) increase, up to 20% compared to the racemic polymers. Said increase is even more formidable knowing that only a fraction of chiral helicene is needed in the main chain (down to 1%) to get higher performances compared to the homopolymers.

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KEYWORDS: Helicene, Chirality, Conjugated Polymers, Optoelectronic Devices, OPV

NON-COVALENT INTERACTIONS IN NEUTRAL
TETRATHIAFULVALENS AND THEIR CHARGE TRANSFER
COMPLEXES

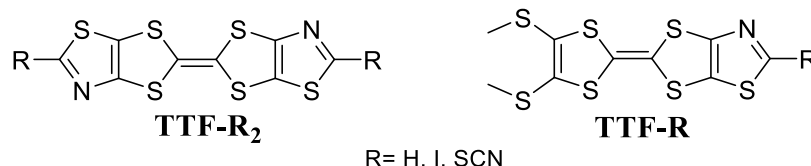
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Abstract

The design and synthesis of tetrathiafulvalene (TTF), a fascinating family of electron donor molecules, continues to receive sustained attention as precursors of conducting materials and their associated broad range applications.¹ The properties of molecular materials are essentially linked to the organization and the interactions of the molecules in the solid state. Thereby, with the aim of gaining control over the solid state organization, the use of non-covalent intermolecular interactions can be envisioned. Herein we investigate the synthesis of novel substituted TTFs able to form non-covalent intermolecular interactions, such as hydrogen, halogen, or chalcogen bonding. For that purpose, we designed fused dithiole-2-one/thiazole derivatives, which under homocoupling led to symmetrically substituted TTFs (TTF-R₂) or through heterocoupling to dissymmetrically substituted TTFs (TTF-R).² The electrochemical investigations allowed the assessment of the electronic effect of these substituents on the overall donating ability of the TTFs. The synthesis and the non-covalent interactions observed with the neutral TTFs and two charge transfer salts obtained with TCNQF₄ as the electron acceptor, (TTF-I)₂(TCNQF₄) and (TTF-H)(TCNQF₄) will be presented.



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SYNTHESIS OF P-CONTAINING POLYMETHINE CYANINES

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Abstract

Many cyanine have been reported and used for various of applications either in biomedicine or in material science. Cyanine dyes have the particularity to have a full charge delocalization on an odd number of C- sp^2 between two lateral nitrogen (Fig. 1). Since the 60's, some rare examples of P-containing cyanine dyes ^[1] were reported but the lack of synthetic access induced by phosphorus chemistry did not allowed their democratization like classical cyanine.

In this work, we will describe our efforts to synthesize different P-containing polymethine cyanines thanks to new procedure. ^[2] We will also investigate the use of different ways of synthesis inspired by classical cyanine ^[3-4]. In particular, we will use the possibility to tune the electronic density on the P-atom to modulate the optical/redox properties.

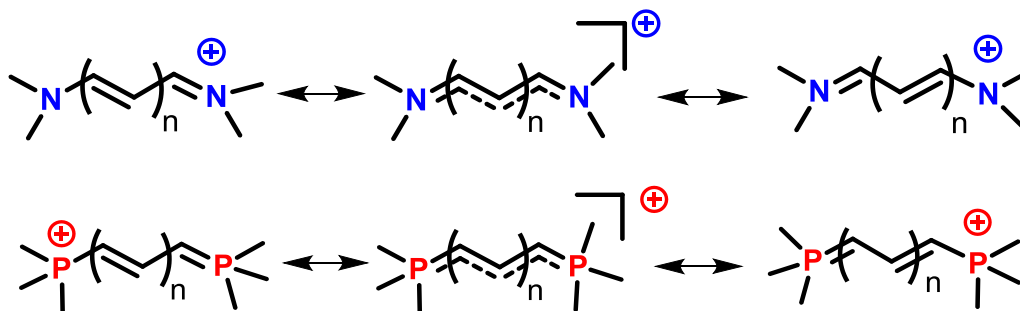


Fig. 1 Classical representation of cyanines / phosphacyanines

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**Highly Robust and Efficient Blechert-type
 Cyclic(alkyl)(amino)carbene Ruthenium Complexes for
 Olefin Metathesis**

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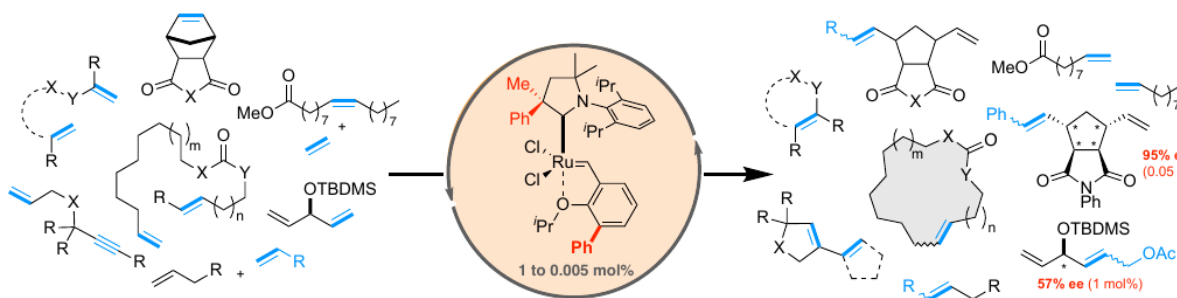
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Abstract

The first Blechert-type ruthenium complexes containing cyclic(alkyl)(amino)carbene (CAAC) ligands are reported. These catalysts demonstrate remarkable thermal stability in solution and excellent catalytic performances at low catalytic loading (up to 0.005 mol%) in ring-closing metathesis (RCM), macro-RCM, ring-closing enyne metathesis (RCEYM), cross-metathesis (CM), ethenolysis and ring-opening cross metathesis (ROCM). Moreover, up to 95% *ee* was obtained in asymmetric ring-opening cross metathesis (AROCM) and 57% *ee* in asymmetric cross-metathesis (ACM).



**Synthesis, reactivity and optical/redox properties of an original
azaaromatic scaffold: the Tetrazo[1,2-b]indazoles**

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Abstract

Keywords: Heterocyclic chemistry, Tetrazine, chromophore, fluorophore, redox properties

Summary: N-rich heteroaromatic rings possess fascinating optical and redox properties and have thus been applied in optoelectronics. While studying the reactivity of orthosubstituted s-Tetrazine[1-2] (molecule A, Fig. 1), we recently observed an unusual cyclization process with azide leading to novel azaaromatic scaffolds : symmetric an non-symmetric Tetrazo[1,2-b]indazoles (B, C, D, Fig. 1) [3]. The discovery of this unique heteroaromatic system opens the door to a colorful chemistry. In this poster, we will discuss the synthesis of this novel pi-system, its reactivity (nucleophilicity, coordination chemistry, etc) and its optical and redox properties.

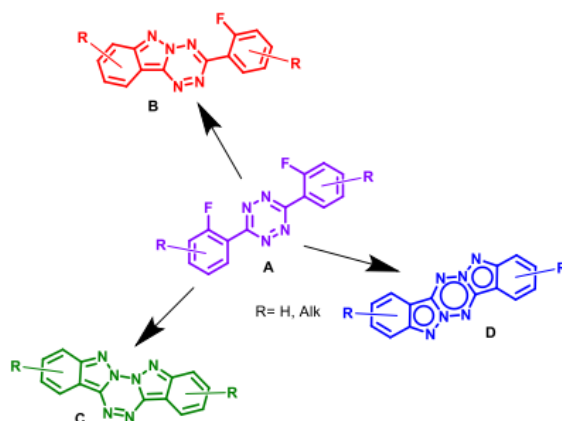


Figure 2: Different Tetrazo[1,2-b]indazoles obtained from Tetrazine A

Références :

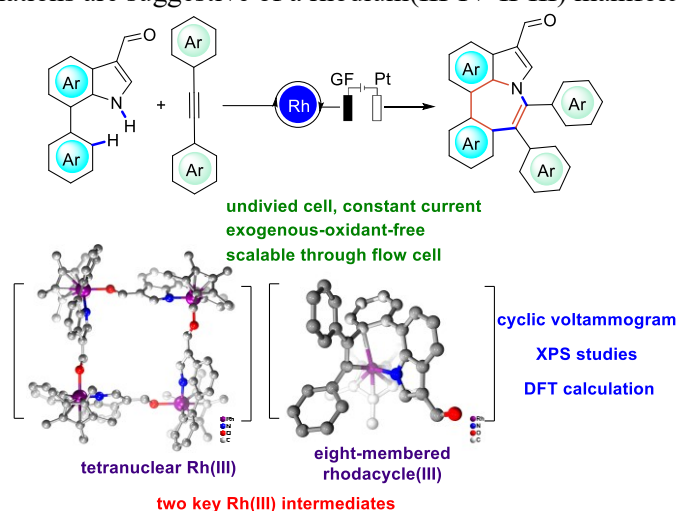
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Scalable Rhodaelectro-Catalyzed Expedient Access to Seven-membered Azepino[3,2,1-hi]indoles via [5+2] C-H/N-H Annulation

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Abstract

A rhodaelectro-catalyzed [5+2] N-H/C-H oxidative annulation of alkynes by 7-arylindoles has been accomplished, enabling the synthesis of seven-membered azepino[3,2,1-hi]indoles using electricity as the sole oxidant. The reaction can be scaled up to gram-scale by flow-electrocatalysis. Two key rhodium(III) intermediates were isolated and fully characterized. Cyclic voltammogram analysis, XPS studies and DFT calculations are suggestive of a rhodium(III-IV-II-III) manifold.



Nanofiltration membrane separation processes in organic solvent media for olefin hydroformylation; membrane cascade optimization for eco-efficient separations.

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Abstract

Olefins hydroformylation is a homogeneous catalytic reaction in which aldehydes are obtained from olefins using a catalytic system composed of a catalyst precursor such as Rh(acac)(CO)₂ and a ligand in excess (here PPh₃).

At the industrial level, the recovery of the homogeneous transition metal catalysts is carried out by distillation which generates thermal degradation preventing from its large recycling and high costs in energy consumption.

Organic Solvent Nanofiltration (OSN), an environmentally friendly separation process, is a pressure-driven, membrane-based technique in which separation is carried out at room temperature and at the molecular level.

In the present investigation, the filtration was achieved at laboratory scale with a PDMS (Polydimethylsiloxane, PuramemFlux) membrane on a complex real industrial reaction mixture either without any solvent or with 3 selected added solvents aiming at studying the possible impact of the solvent on the selectivity of the separation.


The performances (membrane flux for productivity and solute rejection for fraction quality) were studied as a function of solvent type, aldehyde (main product) concentration and transmembrane pressure (TMP). The experiments were performed with an EVONIK METCell equipment. The volume reduction ratio was fixed at VRR=2. TMP varied from 10 to 40 bar. The solvents used were toluene, pentane, and cyclohexane. For concentration and retention calculations, gas chromatography (GC-FID) was used.

Experimental results allowed to study the solute/solvent transfer mechanisms through the membrane accounting for classical solution-diffusion model but also for physico-chemical environment impact. This last one was discussed by the mean of the calculation of the global Hansen Solubility Parameter (HSP, δ) as well as its dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h) components for solutes, solvent and membrane to determine the affinity (Ra distance) between all compounds of the system.

As $C_{\text{Aldehyde}}=1\text{M}$, the maximum permeates fluxes were obtained in pentane with $116 \text{ L.m}^2.\text{h}^{-1}$ compared to toluene ($97 \text{ L.m}^2.\text{h}^{-1}$) and cyclohexane ($85 \text{ L.m}^2.\text{h}^{-1}$) at $\text{PTM}=40 \text{ bar}$, in good agreement with the Ra distances between the membrane and the solvents that were : $5.6 (\text{Jcm}^{-3})^{0.5}$, $5.7 (\text{Jcm}^{-3})^{0.5}$, and $5.9 (\text{Jcm}^{-3})^{0.5}$ for pentane, toluene and cyclohexane, respectively. However, the minimum aldehyde rejection close to 30% was reached whatever the solvents at $\text{TMP}=10 \text{ bar}$ and $\text{VRR}=2$. While the maximum rejection of the PPh₃ ligand was about 50% no matter the solvent at $\text{TMP}=40\text{bar}$ and $\text{VRR}=2$. The accurate determination of the catalyst in the permeate/retentate stream is in progress but seems to be better than 80% knowing that of the PPh₃ presence in a sufficient amount will be determining value for the catalyst stability.

Without any solvent or when the amount of aldehyde exceeded the amount of solvent (close to 3.0-3.9 M), the rejections were significantly different, and negative rejections were sometimes observed. Besides the classical solution-diffusion model, HSP and Ra between solutes and membrane were used to discuss these behaviors.

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