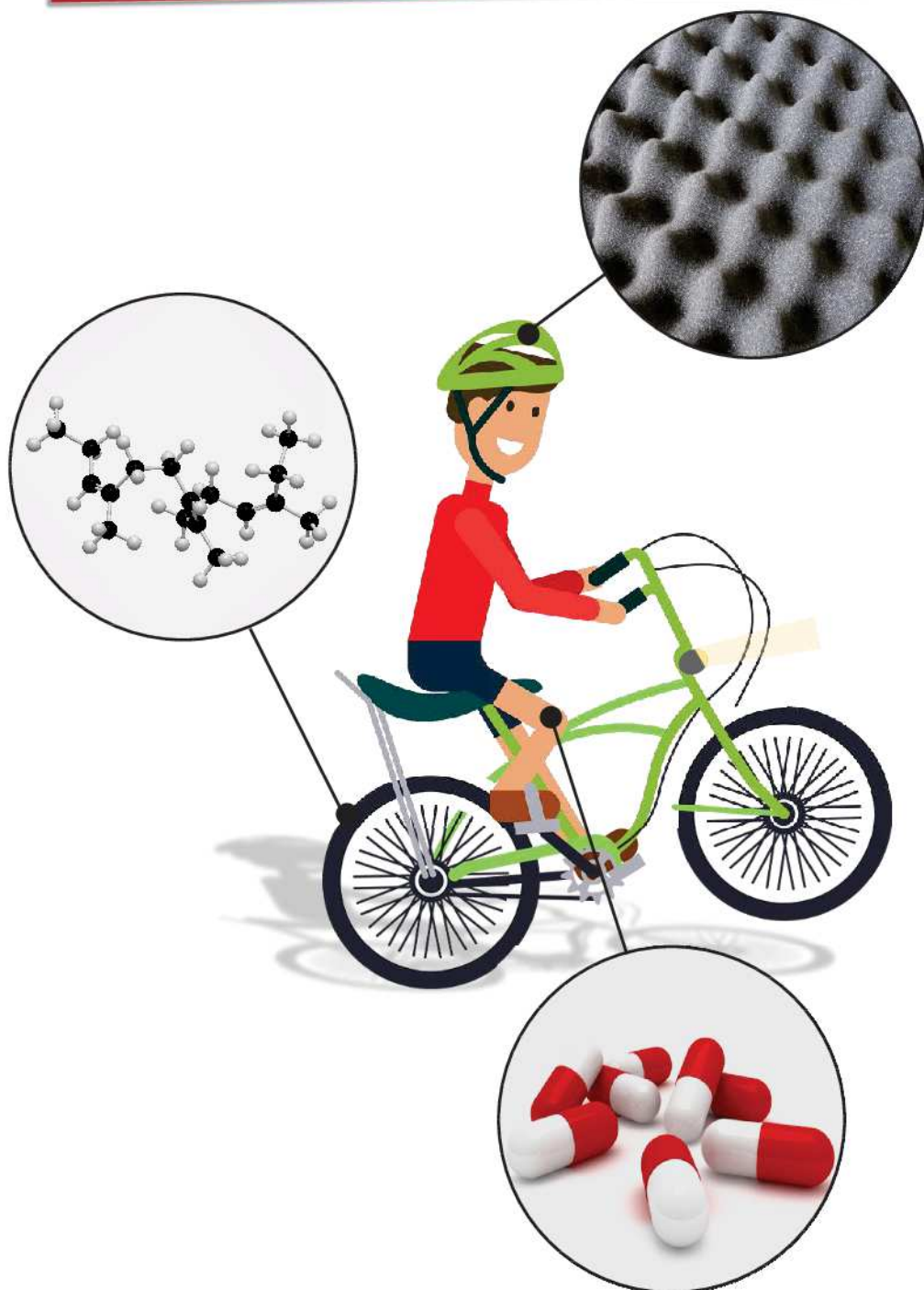


Journée de l'École Doctorale 3M 2018

Molécules et matériaux au service du quotidien



Communications
orales et posters
des doctorants

Échanges autour du
devenir des docteurs



Prix de communication
orale et poster



Société Chimique de France



Société Française
de Physique



Lundi 29 Octobre 2018
8h30 - 17h30
Université de Rennes 1
Campus de Beaulieu
Bâtiment 2A

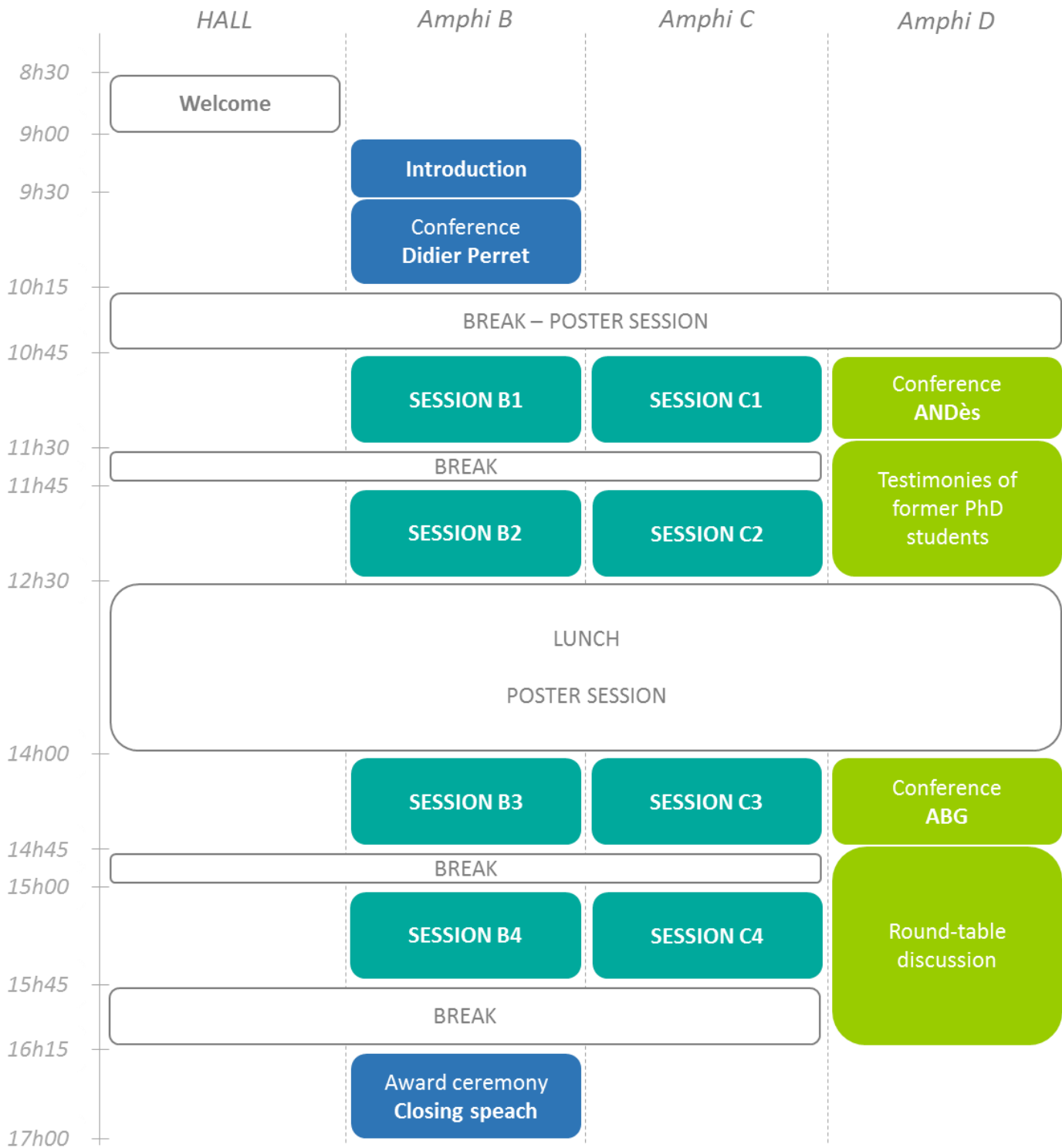
Conférencier invité :

Dr. Didier PERRET

Chimiscope, Université de Genève



Schedule



- Plenary sessions
- Oral communications
- Professional insertion



Fondation

Fondation Rennes 1

Société Chimique de France (SCF)



Société Chimique de France



Société Française
de Physique

Société Française de Physique
(SFP)

Oral communications

AMPHI B

SESSION B1

- 10h45 **LOU Yaoyin**
Coupling of electro-Fenton and electroreduction to improvement of herbicide biodegradability
- 11h00 **BARDOUIL Arnaud**
Osteosarcoma, structure and simulation
- 11h15 **CLAVIER Batiste**
Copper substituted magnesium oxide as biocidal agent in textiles

SESSION B2

- 11h45 **RAMZI Asma**
Study of the welding phenomenon in contactors for aeronautical application
- 12h00 **KHLIFI Soumaya**
Deep-red emitting nanocomposite for integrated broadband 1D-sources
- 12h15 **RALAIARISOA Velotiana Jean-Luc**
Aeolian transport over wet sand beds

SESSION B3

- 14h00 **NIGRON Etienne**
Setting up an accurate measurement method for production cross section: toward an optimized production of radionuclide for medical applications
- 14h15 **OMER Elsa**
Sample preparation for the determination of NIAS in vegetable cans in a chemical food safety context
- 14h30 **JAHJAH Walaa**
 $\text{BiFeO}_3/\text{Ni}_{81}\text{Fe}_{19}$ nanostructured polycrystalline bilayer as a multiferroic candidate for magnetic data recording

SESSION B4

- 15h00 **Mathieu CIANCONE**
Study of photothermal properties of metal bis(dithiolene) complexes in NIR: application for photothermal therapy and photocontrolled drug delivery
- 15h15 **RIO Sandra**
Influence of crystalline phases on optical characteristics of a glass-ceramic in the visible range
- 15h30 **HALZOUN Nadia**
Effect of co-solvents on the Lanreotide self-assembly in water

Oral communications

AMPHI C

SESSION C1

- 10h45 **GAO Jingjun**
New (Ti-Zr)-based superelastic alloy for biomedical applications
- 11h00 **HOUDOUX David**
Study of the link between microscopic and macroscopic scales of plasticity in granular materials
- 11h15 **EL BERJAWI Rayane**
New developments in perylenediimide (PDI) chemistry

SESSION C2

- 11h45 **MENDY Jonathan**
New copper(II) PET/PDT probes for potential cancer theranostic
- 12h00 **EL CHEIKH Aicha**
Monitoring the hardening kinetics of glass-ionomer cements using temporal correlation of speckle patterns
- 12h15 **BOURAOUI Amal**
Amphiphiles for gene delivery influence of the lipid chain

SESSION C3

- 14h00 **MEYER Thibaut**
Etching of chalcogenide glasses using SF₆ plasma
- 14h15 **UTRERA-MELERO Raquel**
Luminescent mechanochromic copper iodide clusters
- 14h30 **FERNANDEZ Maxence**
Hybrid self-assembly of quantum dots and gold nanoparticles driven by protein pairing

SESSION C4

- 15h00 **GRENIER Laura**
Tetraazamacrocyclic-based chelates for single cell analysis
- 15h15 **PIEL Henri**
On the absolute definition of scattering phase shifts in van der Waals systems
- 15h30 **BRÉVALLE Gaëlle**
1.5 μM quantum dots spectral hole burning experiments for dual frequency laser engineering

Professional insertion

AMPHI D

Conférence

10h45

« Comment réussir son doctorat sans anti-dépresseur ? »

Pascal CREPEY – *Ancien président de l'Association Nationale des Docteurs (ANDès)*



Témoignages d'anciens doctorants

11h30 **Julien BOIXEL** – *CNRS*

Roland CONANEC – *CBB-Capbiotek*

Marie POSTIC – *Groupe Onepoint*

Antoine PRIMEL – *Cooper Standard*

Conférence

14h00

Association Bernard Gregory (ABG)

Vincent MIGNOTTE – *Président de l'ABG*

Cette conférence traitera du projet professionnel, des emplois accessibles avec un doctorat et des attentes des entreprises



Table-ronde

14h45

« Projet professionnel, ou comment croiser aspirations professionnelles, attentes des entreprises et connaissance du marché de l'emploi »

Animé par : **Sylvain COLLONGE** – *Responsable de la Mission Recherche à l'Université Bretagne Loire (UBL)*

Jean-François CARPENTIER – *Vice-président de la commission de la recherche du conseil académique de l'Université Rennes 1*

Roland CONANEC – *CBB-Capbiotek*

Pascal CREPEY – *Ancien président de l'ANDès*

Didier FLONER – *Co-fondateur de Kemiwatt*

Vincent MIGNOTTE – *Président de l'ABG*

Antoine PRIMEL – *Cooper Standard*

Abstracts

Oral communications

OSTEOSARCOMA, STRUCTURE AND SIMULATION

A.Bardouil¹, F.Artzner¹, F.Redini², J.Amiaud², T.Bizien³ and A.Fautrel⁴

¹ Institut de physique de Rennes 263 avenue du Général Leclerc 35042 Rennes Cedex

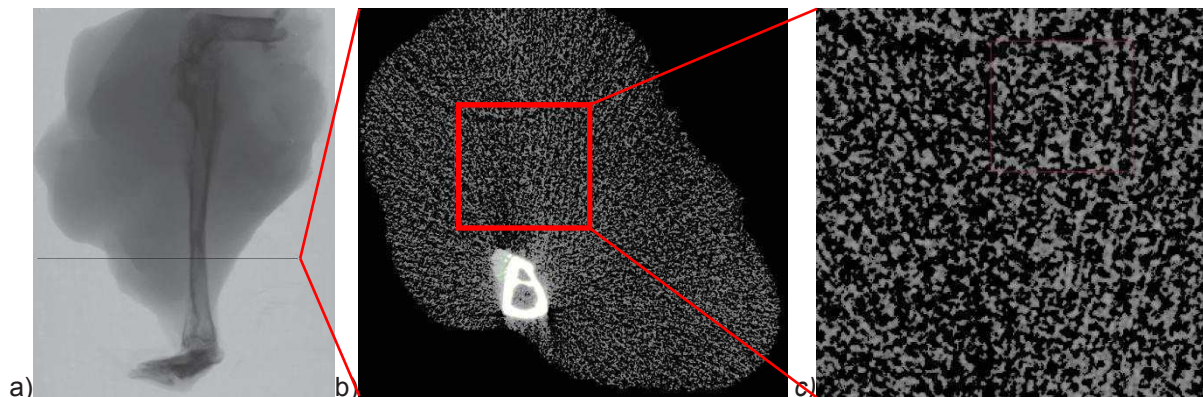
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Osteosarcoma is a malignant bone tumor characterized by an invasive bone and tumor growth that mainly affect teenagers and young adults. It requires extremely invasive surgery to extract, and still displays a 75% mortality rate two years after removal.

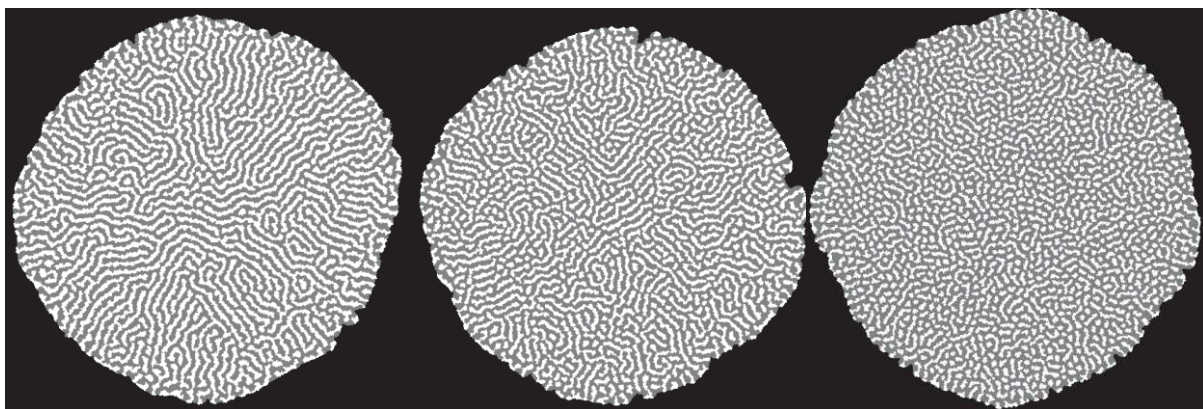
Bone tumor offers a structure that can be studied through physics science means, and using those we strive to study this kind of tumor using a new approach of focusing on the short development times, by opposition to biology's approach of studying well-developed long times samples. Through these observations, we hope to develop a physical model of osteosarcoma propagation using simple laws.



a) Radiography from an osteosarcoma infected mouse leg b) Tomography slice of previous sample
c) Zoom-in of b)

We studied samples from nude rats at 7 and 13 days after osteosarcoma cells injection through Small Angle X-ray Scattering (SAXS) on the Soleil synchrotron in search of a difference in structure between infected and control samples. We observed a noticeable difference between the samples at 7 and 13 days in the amount of oriented bone produced, demonstrating a process of bone fabrication and resorption.

In parallel, to explore the laws ruling osteosarcoma expansion, we developed a simulation process to try and reproduce osteosarcoma structures through simple laws.



Simulation results

So far, we are exploring the possibilities of a Turing interaction model between the bone and sarcoma to produce simulation results approaching the observed structure.

AMPHIPHILES FOR GENE DELIVERY INFLUENCE OF THE LIPID CHAIN

Amal BOURAOUI,¹ Mathieu BERCHEL² Olivier LOZACH³ Rosy GHANEM Laure DESCHAMPS⁴
Véronique VIE⁵ Paul Alain JAFFRES⁵ Tristan MONTIER

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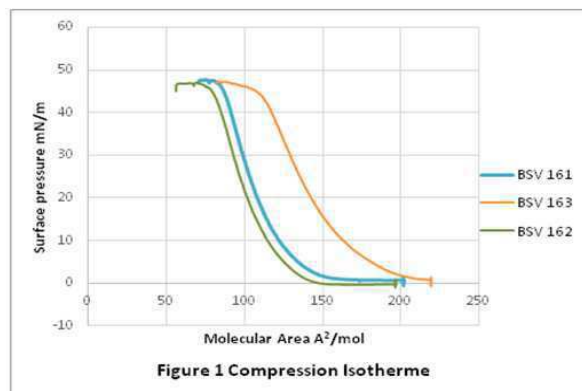
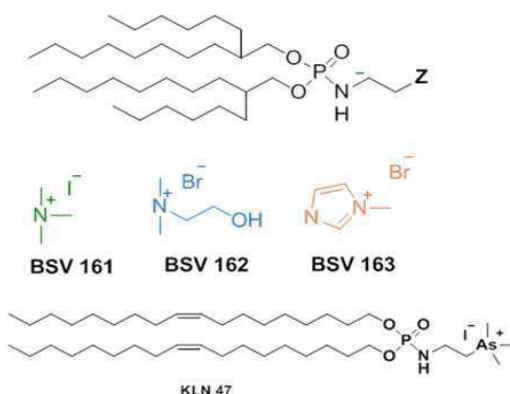
Gene therapy can be defined as the introduction of nucleic acid (DNA or RNA) into human cells in order to prevent or treat different types of illnesses (cancer, cystic fibrosis or tendon healing...). Unfortunately this new therapeutic approach faces many hurdles linked primarily to the polyanionic and hydrophilic nature of DNA molecules.

The use of gene carriers can therefore be a good strategy to overcome these problems. Although they are the most commonly used in clinical trials, viral vectors are costly and difficult to produce; their harmful side effects (toxicity and immunogenicity) are also a major drawback.

Non viral vectors mainly polymers and cationic lipids are considered as the best alternative for viral gene therapy since they are safer, cheaper and easier to produce.

Since the description of the first cationic lipid designed by Felgner and al^[1], a wide library of synthetic vectors has been described but the need for more efficient gene carriers is still on demand. To achieve this goal our team in Brest opted for the strategy of modulating the three building blocks of cationic lipids by changing: [i] the cationic polar head^[1], [ii] the spacer used to join the hydrophobic and hydrophilic moieties^[2] and [iii] modulation of the hydrophobic domain^[3] by changing the size, the symmetry and including ramification whether by using naturally ramified chains like phytanyl or synthesized chains using thiol-ene click reaction.

Herein we present the synthesis of a new family of cationic lipid containing a naturally ramified hydrophobic chain (2-hexyl-1-decanol). These new molecules differ by the nature of their polar head group.



The transfection efficacy of these novel cationic lipids has been studied and compared to KLN 47 and showed excellent transfection results. Furthermore, using compression isotherm we were able to demonstrate that the nature of the polar head group has an influence on the molecular area occupied by the molecules.

We have also used solid state NMR to show that increasing the volume of the hydrophobic moieties has led to inverted hexagonal phase which is known to improve the transfection efficiency of cationic lipids.

References:

- [1] Tony Le Gall, Mathieu Berchel Arsonium-Containing Lipophosphoramides, Poly-Functional Nano-Carriers for Simultaneous Antibacterial Action and Eukaryotic Cell Transfection. *Adv Health Mater.* 2013; 2(11):1513-2
- [2] Aurore Fraix, Tony Le Gall, Mathieu Berchel, Cationic lipophosphoramidates with two disulfide motifs: synthesis, behaviour in reductive media and gene transfection activity. *Org Biomol Chem.* 2013; 11(10):1650-8
- [3] Le Corre S, Berchel M. Cationic lipophosphoramidates with two different lipid chains: synthesis and evaluation as gene carriers. *Org Biomol Chem.* 2014; 12(9):1463-74

1.5 μm QUANTUM DOTS SPECTRAL HOLE BURNING EXPERIMENTS FOR DUAL FREQUENCY LASER ENGINEERING

G. Brévalle^{1*}, M. Perrin¹, C. Paranthoën¹, Y. Léger¹, C. Levallois¹, H. Folliot¹, M. Alouini¹

¹Univ Rennes, INSA Rennes, CNRS, Institut FOTON – UMR 6082, F-35000 Rennes, France

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The Terahertz (THz) frequency domain is attractive for numerous applications including phonon spectroscopy, radio-astronomy, imaging, sensing and communication. Nevertheless the development of a compact, tunable, electrically driven room-temperature source operating in the THz band frequency [1-5 THz] remains a challenge. An alternative to low-temperature-cooled Quantum Cascade Lasers is the widely investigated photomixing technique which relies on semiconductor antenna fed by two laser fields beating at the targeted THz frequency. When a highly coherent CW emission is mandatory, a single laser cavity sustaining the oscillation of the two required laser fields is a very attractive approach. Indeed, the phase noises of the two optical fields being inherently correlated, the beatnote exhibits a high spectral purity. Following this paradigm, dual-frequency Quantum Wells (QWs) based Vertical External Cavity Surface Emitting Lasers (VECSELs) architectures have been successfully demonstrated [1][2][3]. Nevertheless, because of the inherent homogeneously broadened gain of QWs, the two laser modes suffer from strong coupling making it necessary to lift the spatial degeneracy inside the active medium. Moreover, the frequency detuning remains lower than in Quantum Dots (QD).

Accordingly, we have been exploring over the past years the benefits of using wider and potentially less homogeneously broadened gain medium such as Quantum Dots [4]. To this aim, InAs QDs are grown on InP (311B) substrate, and characterized by photoluminescence and atomic force microscopy. The density (from 10^{10} to 10^{11} cm^{-2}) and the size of QDs are carefully engineered while keeping a 1550 nm emission wavelength as shown in Figure 1. To evaluate the potential of QDs for dual frequency oscillation, a critical parameter is the homogeneous linewidth. It is measured through Spectral Hole Burning (SHB) experiments using two tunable and continuous-wave lasers. In order to be as close as possible to the laser operation conditions, the SHB experiments are performed at high temperature levels and high carrier densities.

In this talk, we will present our preliminary results from Spectral Hole Burning experiments conducted on both InAs/InP QDs and conventional InGaAs/InP QWs. The dedicated homemade measurement apparatus will be presented as well.

This work is supported by the IDYLIC ANR project (ANR-15-CE24-0034-01).

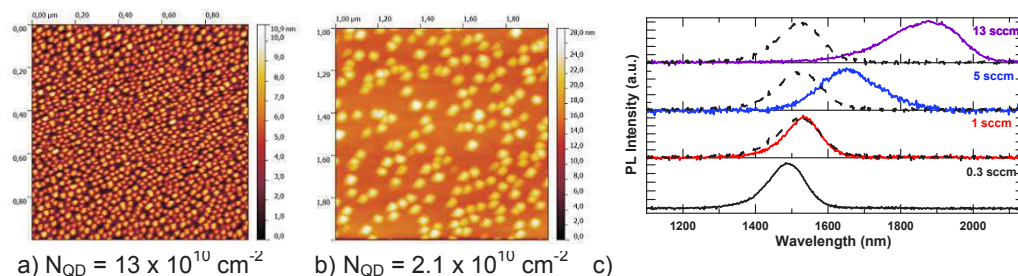


Figure 1 : a) and b) AFM images of InAs/InGaAsP/InP QDs for AsH_3 flows of 0.3 and 13 sccm respectively. c) PL spectra for simple and double cap on QDs (continuous or dashed lines). From bottom to top, the AsH_3 flows are 0.3, 1, 5 and 13 sccm.

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STUDY OF PHOTOTHERMAL PROPERTIES OF METAL-BIS(DITHIOLENE) COMPLEXES IN NIR: APPLICATION FOR PHOTOTHERMAL THERAPY AND PHOTOCONTROLLED DRUG DELIVERY

M. Ciancone¹, K. Mebrouk¹, N. Bellec¹, C. Le Goff-Gaillard², Y. Arlot-Bonnemains², T. Benvegna^c, M. Fourmigué¹, S. Cammas-Marion¹ and F. Camerel¹

¹Université Rennes 1, UMR-CNRS 6226, ISCR (Institut des Sciences Chimiques de Rennes), 261 Avenue Général Leclerc, F-35700, Rennes, France

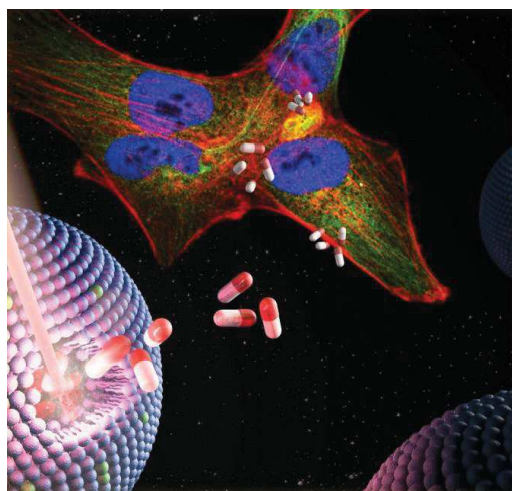
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Metal-bis(dithiolène) complexes have proven being thermally stable and show a large absorption in near infrared with a high extinction coefficient ($30\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$)^{1,2}. These compounds being non-luminescent, it undergo non-radiation deexcitation of the absorbed energy, transforming light into heat with a yield of around 40%³.

Moreover, high versatility of the ligands carried by the metallic center allowed us to synthesize and encapsulate hydrophobic analogues in nanovectors such as thermosensitive liposomes or polymer nanoparticles^{4, 5}. We also managed to incorporate in those nanovectors a fluorescent marker (carboxyfluoresceine) and a common anticancer molecule (Doxorubicin) in order to observe release profiles and track them in cellulo. Both cargos have shown passive release as weak as 5% over 3 month in storage condition at 4°C. However, sudden release can be achieved with precise spatio-temporal control when submitting the nanoparticles to short laser irradiation.

Cytotoxicity of the vectors encapsulating photothermally active complexes have also been evaluated on different tumor cell lines. They have shown good biocompatibility for concentration up to $100\ \mu\text{g}\cdot\text{mL}^{-1}$. In addition, local hyperthermia caused by laser irradiation together with the presence of complex led to a drop of cell viability by 80%, demonstrating the high potential of those vectors for photothermal therapy coupled to targeted chemotherapy.

Figure: Illustration showing the release of active pharmaceutical ingredient toward tumor cells after liposome laser irradiation⁴.



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COPPER SUBSTITUTED MAGNESIUM OXIDE AS BIOCIDAL AGENT IN TEXTILES

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Keywords : magnesium oxide, carbonation, hydration, bactericidal activity

Healthcare-Associated-Infections (HAIs) are a major public health issue in hospitals. In 2012, a report of the French Institute for Public Health Surveillance (<http://www.invs.sante.fr/enp>) pointed out that three pathogens are responsible for more than half of the number of HAIs contracted in hospitals : *Escherichia coli* (26%), *Staphylococcus aureus* (15.9%) and *Pseudomonas aeruginosa* (8.4%). These bacteria have developed strong resistances towards antibiotics due to their intense use and misuse in the past 70 years. The person-to-person transmission occurs most of the time by contact with contaminated surface/object as textiles. A way to limit the spread of nosocomial infections is to design coatings able to inhibit the attachment of bacteria (bacteriostatic property) or to kill them (bactericidal property). Certain oxides such as periclase MgO [1-2] and tenorite CuO [3] exhibit bactericidal activity towards these pathogenic bacteria and have long-term geological availability. These oxides could therefore be incorporated in textiles (gowns, bed linens or pillows) in contact with infected patient, thus efficiently reducing the spread of HAIs in hospitals. The increase in health care services delivered at home is being driven by continued efforts at medical cost saving. Since infections can be also contracted at home, one can imagine that those bactericidal agents will also be incorporated in household textiles in the future.

A limited solid solution solely exists within the magnesium rich end of the MgO-CuO phase diagram [4]. Its existence gives the opportunity to potentially exacerbate the activity of synthetic periclase through partial substitution of magnesium by copper (i.e. Mg_{1-x}Cu_xO). However, magnesium oxide is sensitive to both hydration and carbonation in ambient air conditions [5] thus changing the surface state of grains and potentially their biocidal activity. In the present study, the effects of copper substitution, particle size and hydration/carbonation on the activity of periclase towards *Escherichia coli* and *Staphylococcus aureus* have been thoroughly investigated.

References:

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- [2] Makhluif, S., Dror, R., Nitzan, Y., Abramovich, Y., Jelinek, R., Gedanken, A. (2005) Microwave-Assisted Synthesis of Nanocrystalline MgO and Its Use as a Bactericide. *Advanced Functional Materials*, 15 (10), 1708-1715.
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NEW DEVELOPMENTS IN PERYLENE-DIIMIDE (PDI) CHEMISTRY

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Among all members of the polycyclic aromatic hydrocarbon (PAH) family, perylene diimide (PDI) derivatives have been studied more extensively, because of their rigid planar backbones and extended π -conjugation; which exhibit outstanding optical and electronic properties, chemical and thermal stabilities. PDIs have found their great potential in the field of photovoltaic devices, organic field effect transistors, light emitting diodes, near-infrared dyes, and constructing of graphene nanoribbons.^[1,2]

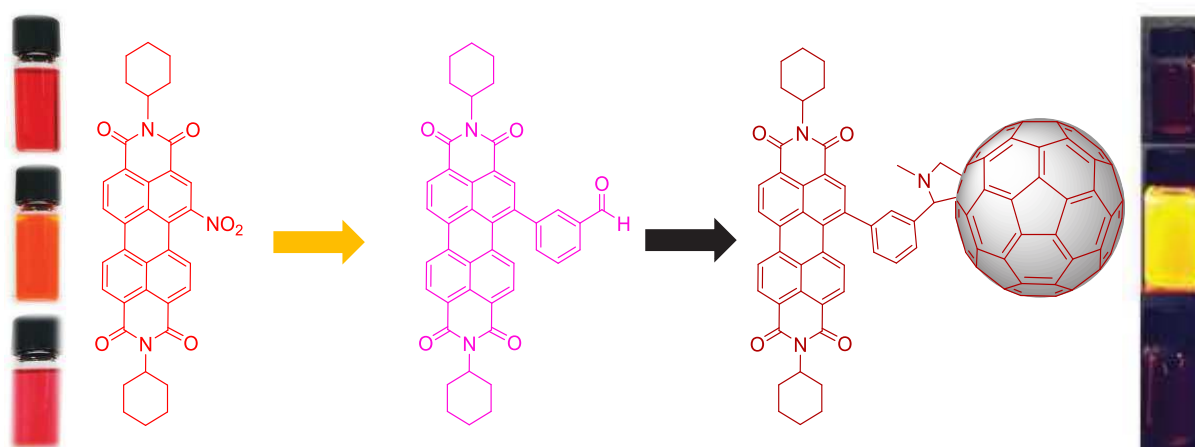


Figure 1. Modified Suzuki-Miyaura cross coupling reaction starting from mono nitroPDI followed by the synthesis of PDI-C₆₀.

Developing core extended PDIs has been strongly sought to further improve their properties, however, their approach suffers from low yields and the lack of structural control, in addition to their strong tendency for π - π stacking due to their planar nature, which leads to a poor solubility in most solvents and to the formation of large aggregates^[1,3,4] In this contribution, we describe the investigation and the control of their reactivity starting, from an electron withdrawing or donating group at the bay region, the mono-nitro and mono-amino PDI. In particular, the development of new methodology for realizing Suzuki-Miyaura cross coupling reactions in addition to Pictet-Spengler condensation. The products obtained could present interesting applications in organic solar cells or photodynamic therapy.

References:

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MONITORING THE HARDENING KINETICS OF GLASS-IONOMER CEMENTS USING TEMPORAL CORRELATION OF SPECKLE PATTERNS

Aicha El Cheikh^{(1) (2)*}, **Fabrice Pellen**⁽²⁾, **Bernard Le Jeune**⁽²⁾,
Guy le Brun⁽²⁾, **Marie Abboud**⁽¹⁾

(1) *Physics department, UR TVA, Faculty of science, Saint Joseph University, B.P. 11-514 Riad El Solh, Beirut 1107 2050; Lebanon*

(2) *Laboratoire OPTIMAG, IBSAM, Université de Bretagne Occidentale, 6 avenue Le Gorgeu, C.S. 93837, 29238, Brest Cedex 3; France*

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Glass-ionomer cements (GIC) belong to the class of materials known as acid-base cements. They harden following an acid-base reaction between basic fluoro aluminosilicate glass powder and an acidic solution of polyacrylic acid [1]. GIC are essential materials in clinical practice mainly because of their versatility, self-adhesion to enamel and dentine, and good biocompatibility [2]. The drying process of these materials and the evolution of their physical properties play an important role in the quality and durability of dental care. Since monitoring these processes contributes to the improvement of the knowledge on these materials, we aim in our work to monitor in real-time the phenomenon of the hardening of GIC using dynamic speckle approach. Speckle is a non-destructive optical technique based on the analysis of variations of laser light scattered from diffusing samples [3]. When the diffusing sample is not static, the speckle activity can reflect its dynamic status. Among the methods that can be used for measuring and analyzing the temporal speckle intensity variations and hence for having a quantitative idea about the analyzed sample activity evolution, one can compute the temporal correlation coefficient $C(t)$ by comparing recorded speckle patterns to the first image of the series [4]. Considered specimens are disk-shaped samples (diameter 1 cm - thickness 2 mm) prepared using precast cartridges from two commercial GIC products (Chemfil® Dentsply and Ketac® 3M) according to NF EN ISO 9917-1. A Helium-Neon laser linearly polarized illuminates the samples and a CMOS camera collects the backscattered light with a rate of 47 fps. The monitoring of GIC hardening phenomenon is performed from the instant when acid and base are mixed ($t = 0$ mn) till 24 hours later. Speckle images are temporally analyzed by computing the temporal correlation coefficient [4]. Numerical fits as well as Fourier transforms show that the temporal correlation curves present a Lorentzian profile as illustrated in figure 1. We use the full width at half maximum (FWHM) of Lorentzian curves as a pertinent parameter to describe the variation of the activity in our specimens. Finally, speckle results are used to determine the setting time of GIC.

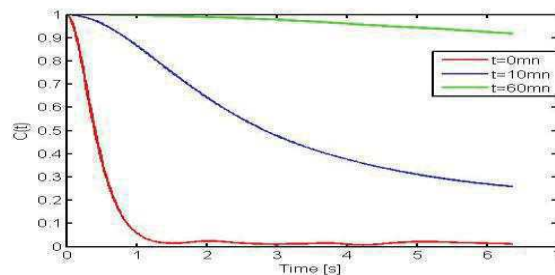


Figure 1: Temporal correlation coefficient curves $C(t)$ between speckle images for GIC Chemfil® during its hardening. The curves at different instants t correspond to various instants during the hardening phenomenon, starting by the instant $t = 0$ mn when acid and base are mixed.

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HYBRID SELF-ASSEMBLY OF QUANTUM DOTS AND GOLD NANOPARTICLES DRIVEN BY PROTEIN PAIRING

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The broad field of nanotechnology has resulted in the design of hybrid nanomaterials featuring exclusive properties such as sensing, data or energy storage and biocide activity. Molecule-driven self-assembly of biomolecules led to the design of colloidal assemblies thanks to the direct recognition of specific molecular partners grafted onto nanoparticles. Direct coupling of nanoparticles has been achieved using DNA strands hybridization, peptide coupling or archetypal protein interactions (streptavidin and biotin) but these methods are either expensive or either restricted to the limits of their assembly mediators.

Recently, novel massive assemblies of gold nanoparticles were designed using artificial repeat protein pairs (α Rep protein pairs).¹ These new and promising assembly agents are able to organize functional colloids and provide control on the interparticle distance. Moreover, α Rep proteins exhibit hypervariable amino acids positions that provide tremendous possibilities of interacting partners such as another protein or a specific crystalline surface.²

In this contribution, we present the design of new homogeneous and hybrid α Rep proteins driven self-assemblies of semiconductor nanoparticles (Quantum dots, QDs) and gold nanoparticles (nPAu). First, the functionalization strategies of QDs and nPAu consists in using a polycystein peptide before grafting of the artificial proteins. The grafting on both α Rep proteins onto these nanoparticles is characterized using agarose gel electrophoresis showing the saturation of their surface. The affinity of protein-functionalized nanoparticles is then characterized using surface plasmon resonance technique. Mixtures of complementary nanoparticles populations are observed under transmission electronic microscopy and show the formation of large colloidal assemblies. The optical properties of these aggregates are finally characterized by fluorescence spectroscopy. These results give hope to design other hybrid colloidal assemblies in order to be used as new optical nanostructures.

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New (Ti-Zr)-based superelastic alloy for biomedical applications

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Keywords: titanium alloy; recovery strain; recrystallization texture; martensitic transformation

Near equiatomic Ti-Ni alloys are commonly used for biomedical devices such as orthodontic arches, orthopedic staples, endovascular stents..., as shown in Fig.1, due to their high strength, good corrosion resistance and extraordinary superelastic effect. However, Ni hypersensitivity still remains an unsolved problem and Ni-free superelastic β -titanium alloys are now considered as the right alternative option for biomedical applications.

With the aim of obtaining excellent superelastic recovery strain, high strength and very low Young's modulus, a newly developed superelastic Ti-20Zr-3Mo-3Sn alloy (at.%) (Ti2033) was elaborated by cold crucible levitation melting (CCLM) technique under high vacuum. Beta phase transition temperature of as-rolled Ti2033 was measured by electrical resistivity and recovery strain was evaluated through cyclic tensile tests. In the present work, special attention was focused on the influence of crystallographic orientation and grain size distribution on superelastic performance via optimized thermal treatments. As a consequence, a very high recovered strain of 3.5% was obtained after a flash treatment at 700°C for 2 min (FT-700-02). With this thermal treatment, the optimal recrystallized texture and the smallest grain size were obtained in order to maximize the superelastic property of the Ti2033 alloy. By way of illustration, Fig.2 shows the cyclic tensile test curve with 3.5% recovery strain (a), an inverse pole figure (IPF) map obtained by electronic backscatter diffraction (EBSD) technique (b) and the corresponding IPF of the flash treated Ti2033 alloy (c).

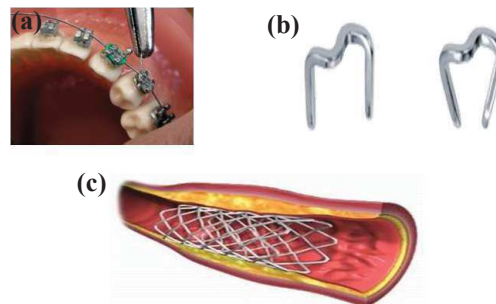


Figure 1 : The applications of Ti-Ni alloys in our daily life: (a) orthodontic arches; (b) Osteosynthesis staples; (c) stents

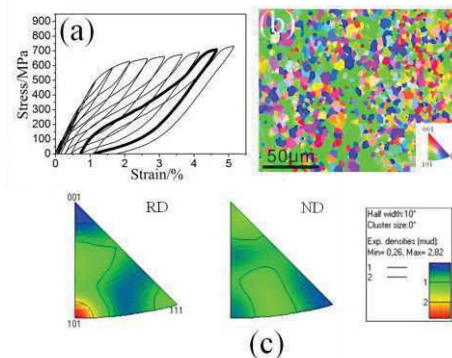


Figure 2 : (a) Engineering stress-strain curves obtained from cyclic tensile test at room temperature; (b) EBSD IPF map; (c) IPF for the Ti2033 alloy (FT-700-02)

TETRAAZAMACROCYCLIC-BASED CHELATES FOR SINGLE CELL ANALYSIS

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Recently, personalized medicine has known a huge success especially in cancer treatment. Yet, personalized treatments are limited and often not a routine solution. To apply target-specific therapy, doctors and biologists need to identify the responsible anomaly for the disease by knowing the entire phenotype, or profile, of the diseased cells. To be able to perform reliable and deep profiling of cells, analysis must be run on a single cell level and recover expression rate of as many parameters as possible in one experiment. Any protein that can be immunotargeted is a parameter.

Mass CyToF (Cytometry Time-of-Flight) technology enables high sensitive measurements and multiparametric analysis of cell suspensions, allowing researchers to better characterize and understand proteomic complexities of heterogeneous cell populations. In this technique, cells are immunostained with antibodies labelled with isotopic metal cations, which are detected by a mass spectrometer [1] (Figure 1). The high resolution and sensitivity of the apparatus allow the analysis and the quantification of various cell surface markers without interferences between tags. The large amount of metal isotopes available in nature would enable the simultaneous analysis of 75-80 parameters.

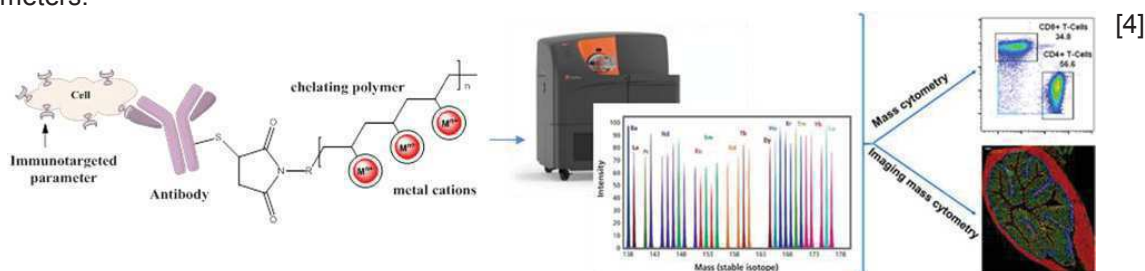


Figure 1. Mass cytometry principle

Mass cytometers developed by Fluidigm Inc. are currently capable of analyzing 37 parameters in a single assay, which is twice more than the commonly used flow cytometry technique. Fluidigm biomarkers performance relies on a metal-chelating polymer attached to the antibody via a maleimide linker. The water-soluble polymer backbone increases the number of metals, which can be introduced and thus detected [2].

In order to take advantage of mass cytometry, new metal isotopes must be used and therefore metal-specific chelators must be designed. Tetraazamacrocycles are well-known to specifically complex a large variety of metals and to form kinetically inert and thermodynamically stable complexes with metal cations [3]. Additional reacting groups can be added on the macrocyclic backbone of these chelates, what is called C-functionalized, and they so present an anchor function for the grafting on the polymer, themselves conjugated on specific antibodies (Figure 2). The numerous challenges will be discussed.

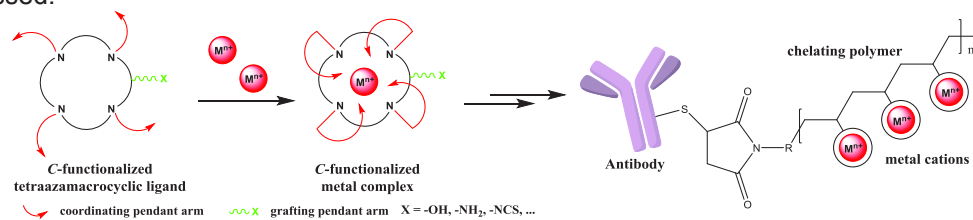


Figure 2. Tetraazamacrocyclic-based chelates

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Effect of co-solvents on the Lanreotide self-assembly in water

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Self-assembly is an ubiquitous process in nature. It governs the spontaneous supramolecular organisation of biological systems such as membranes, cytoskeleton, DNA double helix and protein folding through noncovalent interactions¹. Peptides are oligomers of amino acids linked by amide bond. They are versatile and simple building blocks to design self-assembling nano-architectures such as nanotubes, spheres, ribbons or fibers^{2,3}.

In this presentation, a model of pharmaceutical peptide self-assembly is discussed. Lanreotide is a dicationic octapeptide which forms more or less viscous gels in water³. Its secondary β -hairpin structure is cyclised by disulfide bridge⁴. In pure water, Lanreotide (10% w/w) self-assembles in nanotubes with a diameter of 24.4 nm, a wall thickness of 1.8 nm and few hundred micrometers length. The wall of the nanotubes forms a bi-dimensional crystal. The self-assembly of Lanreotide is ruled by its amphiphilicity through hydrophobic and hydrophilic faces of the β -hairpin. The nanostructures are stabilized by non-covalent interactions : hydrophobic effect, Hydrogen bond, aromatic interactions and electrostatic repulsions^{4,5,6}. The counterion substitution, the addition of co-solvents (e.g. Polyethylene glycol (PEG)) and the mutation of some residues decrease the diameter of the nanotubes^{4,6}. Moreover, the addition of co-solvents (e.g. PEG and *N*-methyl-2-pyrrolidone) significantly changes the viscosity.

We investigated the effect of co-solvents like *N*-methyl-2-pyrrolidone (NMP), ethanol and acetic acid on the supramolecular self-assembly of the Lanreotide in order to understand the molecular mechanism of the transformations. For this purpose, a multi-technics method (X-ray diffraction (SAXS), polarized microscopy and vibrational spectroscopies (ATR-FTIR)) was combined.

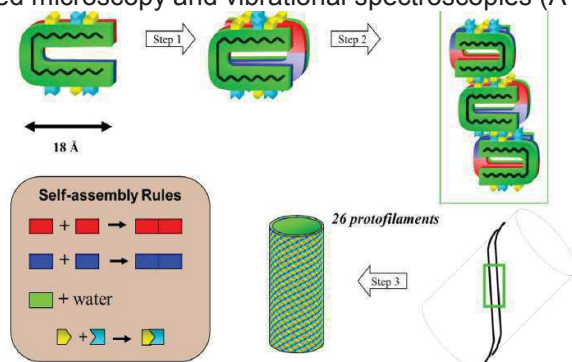


Figure 1 : Self-assembly of Lanreotide; Hydrophilic face in green; hydrophobic face in red (aromatic residues) and blue (aliphatic residues) and hydrogen acceptor and donor in yellow and turquoise

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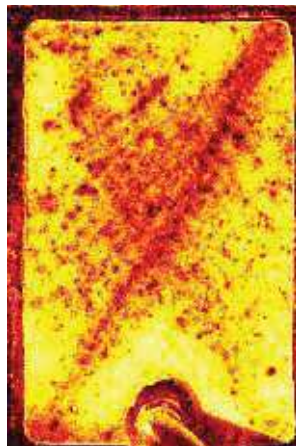
STUDY OF THE LINK BETWEEN MICROSCOPIC AND MACROSCOPIC SCALES OF PLASTICITY IN GRANULAR MATERIALS

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Granular media are systems consisting in a large amount of macroscopic particles having a typical size greater than 100 microns. These systems are extremely diverse and widespread in industry, civil engineering, geophysics or even in our houses. Granular media can be sand, rock, track ballast, drugs or cereals. In the context of their use or in nature, these materials can undergo high stresses leading to irreversible deformations. Thus, it is a key issue to know their value of yielding stress and their behavior beyond this threshold. Current research are focused on the microscopic origin of deformations in order to anticipate and prevent the failure of these granular materials.

In the laboratory, the plasticity (i.e. irreversible deformations) of these materials is studied experimentally using the biaxial test technique on a model granular medium. Microscopic deformations within the system are visualized and quantified using a speckle interferometry technique and correlation calculations. Compare to the macroscopic scale, a different microscopic behavior is observed and quantitatively analyzed in order to establish a link between these two scales. Moreover, each behavior can be related to a theoretical model.



Visualization of irreversible microscopic deformations (black dots) in a correlation map from speckle images.

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BiFeO₃/Ni₈₁Fe₁₉ NANOSTRUCTURED POLYCRYSTALLINE BILAYER AS A MULTIFERROIC CANDIDATE FOR MAGNETIC DATA RECORDING

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Electrical control of magnetic nanostructures would create a new generation of electronic devices directly integrable in actual device architecture.¹ For the last decades a great deal of research has been focused on an efficient way to control magnetic properties using an electric field, with no need of an applied magnetic field.^{2,3} This research is of importance in the field of applied physics when considering magnetic memories or high frequency devices.⁴ For example, spin polarized current is an effective mechanism to transfer a torque to magnetization, but requires large current densities, leading to energy loss because of Joule heating effects.¹ Among the different possibilities for electrical control of magnetism, the use of single-phase magnetoelectric multiferroics (MMF) is considered, as it allows direct means of controlling magnetization via an electric field in a single heterostructure.⁵ Room temperature MMF are rare. Bismuth ferrite, BiFeO₃ (BFO), is the most studied MMF for both its unique ferroelectric and antiferromagnetic (AFM) orderings well above room temperature.

In order to use an AFM MMF with no net magnetization, a ferromagnetic (FM)/AFM exchange coupling is proposed. It can be introduced by placing the AFM layer in contact with a FM material, and is referred to as exchange bias coupling.⁶ It produces an additional anisotropy that stabilizes the FM layer. Exchange bias is at the base of the GMR magnetic sensors used as read heads in a hard disk drive (HDD), or in magnetoresistive random-access memory (MRAM). The existence of exchange bias coupling is usually revealed by a field shift of the magnetization hysteresis cycle, named exchange bias field H_e , and by an enhancement of the coercive field H_c . Room-temperature exchange bias has already been demonstrated in epitaxial BFO/FM⁷, as well as in polycrystalline thin films.⁸

We report through a systematic experimental study on the direct correlation between the Bi₂O₃ parasitic phase concentration that crystallizes in the BFO and the magnetic properties of the polycrystalline heterostructure BFO/FM=Ni₈₁Fe₁₉ deposited via magnetron sputtering. We find that the macroscopic H_e , that arises from exchange bias coupling, is null for phase-pure BFO, and increases up to 18 Oe with an increasing concentration of Bi₂O₃. This trend is in agreement with the azimuthal behaviour of the in-plane magnetization reversal when rotating the sample in the VSM (Fig.1). This characterization also shows anisotropy contributions variation. Our structural characterization also shows that phase-pure BFO has a disordered mesoporous structure.

These results show for the first time the role of the usually known defects in the BFO/NiFe bilayer (i.e. the parasitic phase Bi₂O₃ and the mesoporous state), on the magnetization reversal and the exchange bias coupling mechanism. Also, the BFO mesoporous state may be of interest for composite materials based on mesoporous structures for strain engineering.⁹

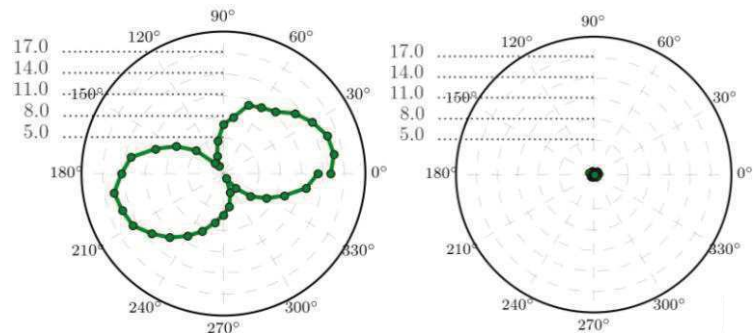


Fig. 1: Azimuthal evolutions of H_e (in Oe) in BFO/NiFe for BFO with (left) and without (right) parasitic phases.

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DEEP-RED EMITTING NANOCOMPOSITE FOR INTEGRATED BROADBAND 1D-SOURCES

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Integrated photonics have become a major research axis for the photonics industry consortium. Currently, the society is in front of hustle applications in computing, storage and communication capabilities. Information traffic is growing by around 50% each year, which explains why industry give such importance to optimize digital information circulation and to develop new systems that are more efficient and more profitable. The use of optical links to replace electrical links would provide a huge gain in bandwidth, power consumption and density. In consequence, collective manufacturing techniques of the microelectronics industry are beginning to be applied for fabrication of photonic circuits, which has led to integrated photonics emergence. This new domain aims to group all photonic components (waveguides, couplers, polarizers, interferometers, sources and detectors) on a same planar III-V semiconductor substrate. However, the use of these semiconductors remains relatively expensive, which push other investigations to avoid the drawbacks and at the same time to be easier to process. Based on that, hybrid organic-inorganic materials combining luminescence and ease of shaping are ideal candidates for the realization of devices applied to integrated photonics.

In this context, we have developed 1D micro- and nano-sources emitting in the red and the near infrared with a broad band (650-800 nm), starting from a nanocomposite organic matrix containing strongly luminescent octahedral clusters of transition metals ($A_2M_6X^i_8X^a_6$ where A: organic or alkali cation, M: Mo or W, X^i : inner ligand, X^a : apical ligand). These clusters have several advantages: a high quantum yield in solid polymer matrices, a large Stokes shift and no photo-bleaching or photo-blinking effects in comparison with other inorganic or organic luminophores emitting in the same wavelength range. The choice of organic polymers to be used was perceived by the adequacy between their optical properties and those of the clusters used as well as by the devices envisaged.

After presenting the synthesis of these new hybrid nanomaterials^[1,2] and their physico-chemical characterizations, we will expose their optical properties and their guiding capabilities once shaped.

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COUPLING OF ELECTRO-FENTON AND ELECTROREDUCTION TO IMPROVEMENT OF HERBICIDE BIODEGRADABILITY

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Herbicides are widely produced and used in agriculture and grasslands application all over the world for the control of weeds. The excess use of herbicides is inevitably found as a residue in the environment surrounding human activity. Most of herbicides are persistent organochlorine compounds which cannot be degraded naturally and are even refractory to the traditional biological processes. It has been reported that the toxicity of organochlorine compounds can be partly attributed to the presence of the chlorine atom(s). Alachlor is one of the extensively used herbicide from chloroacetanilide family for control of annual grasses and broadleaf weeds in crops. The concentration ranges of alachlor detected for example in the Castilla-León (C-L) region (Spain) are over $\mu\text{g/L}$ in surface waters and even in the groundwater [2]. In a first work, we studied the reductive dechlorination of alachlor to improve its biodegradability. It was performed on a Ni layer covered graphite felt modified by silver nanoparticles. A biological treatment in 21 days was then carried out on pure alachlor and the electrolyzed solution. As no mineralization or biosorption was observed for pure alachlor, Mineralization yield of 45% was obtained for the electrolyzed solution. However, the concentration of the main product, deschloroalachlor, was stable during the 21 days of culture, showing that the presence of the chlorine atom is not the only source of alachlor biorecalcitrance. Possibly the amide nitrogen with the alkoxy methyl group in alachlor blocks the biodegradation according to the study of Zhan et al. [5]. Hence, a coupling process including electroreduction as a pre-treatment and electro-Fenton process can be considered to improve the biodegradability. This coupling will be followed by a biological treatment to complete the mineralization. Electro-Fenton process is known as a powerful and unselective treatment, which could oxidize recalcitrant by products such as deschloroalachlor. This coupled process will be compared to the electro-Fenton oxidation of alachlor in terms of mineralization efficiency and biodegradability improvement since an electro-reduction pretreatment could avoid the formation of chlorinated by-products during the non selective electro-Fenton oxidation.

The ratio of biochemical oxygen demand in 5 days (BOD_5) to chemical oxygen demand (COD) was introduced to evaluate the biodegradability of the electrolyzed solutions; a ratio above a limit threshold of 0.4 indicates a readily biodegradability of a solution. First results show that this ratio increased from 0 for the non-treated target compound to 0.25 after the electro-Fenton process and to 0.31 if applying electroreduction prior to electro-Fenton. In this work, we first optimized the different parameters used in the electro-Fenton process and it was found that the maximum alachlor degradation (100% conversion within 15 min) and mineralization (over 90% after 180 min) can be reached when a current intensity of 200 mA was applied in the presence of 0.05 mM of Fe^{2+} catalyst, providing oxygen at 0.3 L/min air flow rate. The best duration of the electrolysis has to be determined to on one hand sufficiently oxidize the target compound to improve the biodegradability and to the other hand to have enough carbon substrate for a further biodegradation. Finally, mineralization with electro-Fenton process, with electro-Fenton coupled to biodegradation and with coupled electroreduction, electro-Fenton and biodegradation will be performed.

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NEW COPPER (II) PET/PDT PROBES FOR POTENTIAL CANCER THERANOSTIC

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Cancer theranostic is an emerging field combining both therapeutic and diagnosis modalities within the same probe and allows a real-time monitoring of treatment progress. In the goal of the conception of bioprobes suitable for a use as Positron Emission Tomography (PET) radiotracers and photosensitizers for PhotoDynamic Therapy (PDT), novel Cu(II)-based cyclam derivatives have been developed.

Radiopharmaceuticals using ⁶⁴Cu are emerging as potential diagnostic agents for PET because of the emission properties of this radioelement ($t_{1/2} = 12.7$ h, $E_{\beta^+} = 656$ KeV). The use of PET-radiometals requires the development of specific ligands able to form highly stable complexes to avoid the release of the radioisotope in biological media.

In this context, our group has reported the promising properties of monocolinate cyclam (**te1pa**) and its reinforced derivative (**cb-te1pa**)⁺ chelators due to their high binding properties toward Cu²⁺ in terms of thermodynamic and kinetic stabilities (Figure 1).^{1,2} Furthermore, the radiolabeled complex ⁶⁴Cu-**te1pa** has proved its stability in human serum and the possibility of specific *in vivo* PET imaging after conjugation to a biological vector.

PDT uses an oxygen singlet photosensitizer which becomes cytotoxic upon light-irradiation. However, current PS mostly absorb in the UV/Visible range, while the tissue transparency is in the near-infrared region (NIR). Two-photon excitation can overcome this drawback by, simultaneous absorption of two lower-energy photons in the NIR. In this context, a two-photon photosensitizer capable to be excited in the NIR and to induced cell death thanks to a good singlet oxygen generation quantum yield was reported.⁴

Our project aims to couple these two modalities in order to develop new Cu(II)-based theranostic bioprobes to target cancer cells. This requires the synthesis of derivatives of **te1pa** and **cb-te1pa** functionalized with a two-photon antenna (Figure 1). The synthesis of these ligands, their Cu(II) chelates ([Cu(L¹)]⁺ and [Cu(L²)]⁺), and their photophysical properties will be presented.

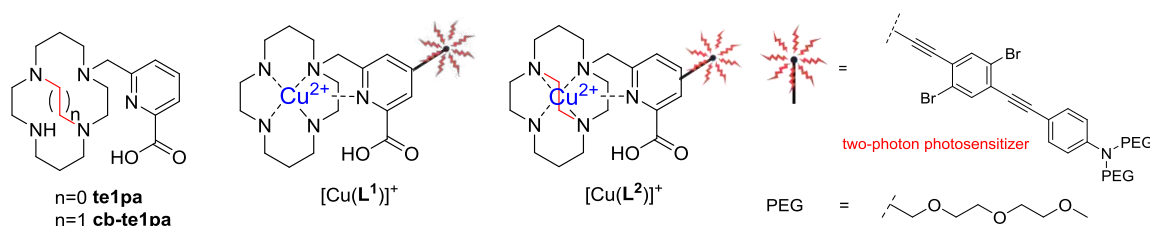


Figure 1. Monocolinate cyclam derivatives and their Cu(II) complexes discussed in this work

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Etching of chalcogenide glasses using SF₆ plasma

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Chalcogenide glasses (ChGs) contain at least one chalcogen element (S, Se, Te), and elements of IV-V column (Ge, As, Sn, Sb...). With a low transmission loss in the infrared region, ChGs are adapted for the fabrication of waveguide in the IR. However, ChGs need a specific shape before these glasses work as waveguides. A rectangular pattern, resulting of an anisotropic etching, with the smallest roughness on sidewall is required to fabricate a waveguide with the fewer transmission losses. Plasma etching is a useful technique which permits to obtain a rectangular pattern on various types of material including ChGs as Ge-Sb-Te, Ge-Sb-S and As-Se.

This study is focused on the etching of Ge-Se and Ge-Sb-Se glasses. An Inductively Coupled Plasma (ICP) reactor allows to control independently the plasma density and the substrate bias. Plasma diagnostics such as optical emission spectroscopy, mass spectrometry and electrostatics probes are performed during the GeSe etching. These measurements provide some understanding about the volatile products, which are SeF₄, SeF₆, GeF₂, and GeF₄, by monitoring neutrals and ions intensities. The interaction between volatile products and SF₆ plasma are directly explained by the variation of plasma parameters measured by the Langmuir probe. Partial pressure, of O₂ or Ar added, do not exceed 50% of the total pressure. In situ X-ray Photoelectron Spectroscopy gives information on composition variation or the oxide formation regarding the etching conditions. Coupled with plasma parameters, SF₆ gas allows to study the effect of wide plasma chemistries on CHGs.

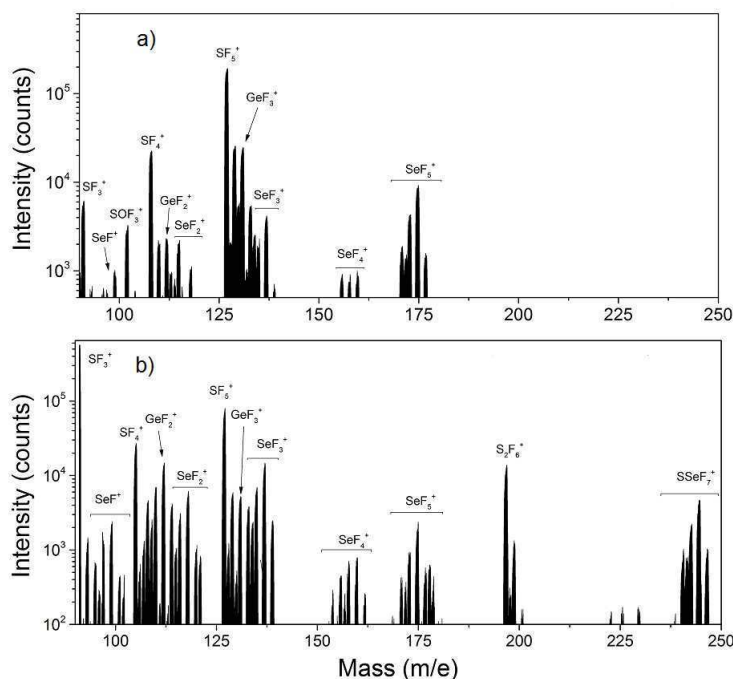


Figure - Mass spectrometry of a) neutral species b) ionic species in SF₆ plasma during the etching of Ge-Se glass.

SETTING UP AN ACCURATE MEASUREMENT METHOD FOR PRODUCTION CROSS SECTION: TOWARD AN OPTIMIZED PRODUCTION OF RADIONUCLIDE FOR MEDICAL APPLICATIONS

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The nuclear medicine is a medical specialty that uses radionuclides for diagnosis or therapy. Several modalities are used in diagnosis (PET/SPECT, Positron Emission Tomography/Single Photon Emission Computed Tomography) which takes advantage of the photon emissions occurring during the decay of the radionuclide. In therapy, strongly interacting particles obtained through the radioactive decay are used such as alpha, beta or Auger electrons. They are mostly used coupled to a vector molecule for targeted therapy. The trend followed by nuclear medicine is to become more and more personalized to each patient. To reach that goal, a wide variety of radionuclides (different decay particles, different half-lives, different chemical properties) must be available to meet the patient's need. Their production is achieved using reactor or accelerator and has to be well controlled.

In order to optimize the production of radionuclides, a good knowledge of the radionuclide production cross section is required. In collaboration with the GIP ARRONAX^[1] which possesses a multi-particle high energy cyclotron, the project is to get an accurate measurement of production cross sections for a wide variety of radionuclides. Among the information requires for a precise measurement, the flux of the incident particle is the more important one. The data about the particle flux of the beam can be evaluated using a monitor reaction with a well-known cross section whose values are recommended by the International Atomic Energy Agency (IAEA). The uncertainty (around 10%) associated to the monitor cross section values results in a high uncertainty on the measured ones. Another method is to measure the amount of charges crossing the stack. This method allows reducing the uncertainty on the measured cross section (<3%). In order to use this technique, a new experimental cross section measurement device has been set up and it is being tested in well-known conditions.

Both techniques of flux determination and final cross section data have been used in a well define example: the production of the ^{197m}Hg (T_{1/2} = 23.8h) which emits only low energies gammas emissions, 70-410 keV with main emissions at 134 keV 33% and 279 keV 6%. These features make the ^{197m}Hg a great candidate for the SPECT imagery. The results obtained reveal that the new experimental set-up works well and the results are in good agreement with the IAEA recommended cross section values and other available data in the literature.

The satisfying results obtained show that this method can be used to measure production cross sections and complete data base for radionuclides of interest.

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SAMPLE PREPARATION FOR THE DETERMINATION OF NIAS IN VEGETABLE CANS IN A CHEMICAL FOOD SAFETY CONTEXT

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Bisphenol A (BPA) is today the compound that everyone has in mind when we talk about plastics chemical contamination issues. Although BPA is often referred to as "everywhere chemicals", the main source of human exposure is through diet, particularly because of its use in food and beverage cans where epoxy-lacquers based on BPA diglycidyl ether have traditionally and extensively been used worldwide. As a consequence of consumer and scientific concerns about possible endocrine disrupting effects, some countries have taken action on BPA and thus phased-out its use. BPA was indeed banned from baby bottles in Canada in 2008, in France in 2010, in all of Europe in 2011, and in the United States in 2012. Further in 2015, France forbid the use of BPA "in any food or beverage packaging". To deal with BPA ban, polyester-based lacquers have grown as serious alternative coatings. Although these alternatives are fully compliant with the direct food contact, it is important to verify that under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health. In particular, besides Intentionally Added Substances (IAS) used in polyester-based lacquers for their technical properties and which monitoring is not considered an analytical challenge, the investigation of the presence of Non-Intentionally Added Substances (NIAS) has been raising the interest of the scientific community. NIAS can be either predictable or unpredictable oligomers (cyclic, linear or branched) originated respectively from known monomers or after reaction between oligomers or monomers with solvent, reticulation or blocking agents used in lacquer formulation. Consequently, faced with such a range of possible chemical structures, identification of NIAS is required as a first step of risk assessment process.

Our recent results [1], using liquid chromatography coupled to high resolution mass spectrometry, already demonstrated the migration of cyclic polyester oligomers from industrial coatings extracted by solvent. Beyond identification, which was the purpose of the first step of the PhD work, the next step addresses the characterisation of such migrating substances in foodstuffs in an exposure assessment perspective.

In the present work, a sample preparation strategy has been developed for monitoring NIAS migrating from polyester-type lacquers to foodstuffs. Vegetables, specifically beansprouts, salsify and corn, were selected as model matrices with few lipid contents. Such food items are very complex and requires a purification step after extraction prior to analysis, aiming at removing interfering compounds. The development of a strategy to both extract and purify NIAS is considered a challenge because of the large range of physico-chemical properties they exhibit (i.e. polarity, size, ...). QuEChERS (**Q**uick **E**asy **C**heap **E**ffective **R**ugged and **S**afe) a dispersive SPE approach, successfully applied in multi-residue analysis (e.g. pesticides analysis in fruits and vegetables [2]) was selected in the present study as the most relevant process for NIAS extraction from drained vegetables. The procedure involves initial single-phase extraction of 10 g sample with 10 mL acetonitrile, followed by liquid-liquid partitioning formed by addition of 4 g anhydrous MgSO₄. Removal of residual water and cleanup are performed simultaneously by using a rapid procedure called dispersive solid-phase extraction (dispersive-SPE), in which 900 mg anhydrous MgSO₄ and 150 mg primary secondary amine (PSA) sorbent are simply mixed with acetonitrile extract. The dispersive-SPE with PSA effectively removes many polar matrix components, such as organic acids, certain polar pigments, and sugars, to some extent from the food extracts. LC-HRMS is then used for NIAS determination.

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ON THE ABSOLUTE DEFINITION OF SCATTERING PHASE SHIFTS IN VAN DER WAALS SYSTEMS

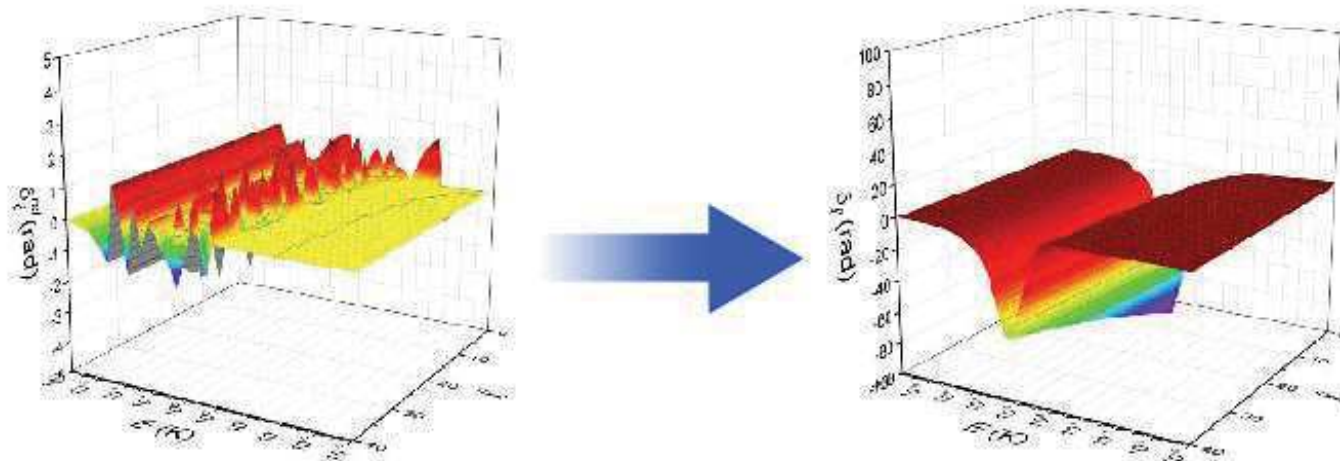
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The notion of phase is commonly used daily, especially in the scientific domain, to account for situations where retardation effects play a major role at a macroscopic scale. In fact, retardation effects are the cornerstone of the analysis of a vast class of scientific inquiry ranging from nuclear physics to astrophysics, including optics and electronics, enabling to explain a variety of physical phenomena of the daily life. These effects usually appear in the form of distance, time as well as angle according to the situation we are dealing with. The latter is commonly called dephasing or phase shift. For instance, in the optical domain, phase shifts can be concealed by the determination of the optical path difference generated by a light beam crossing a glass slide. Another relevant example is the phase delay introduced by an electric dipole filtering a signal in an electrical RC system.

Hence, the determination of phase shifts is usually a critical issue and this is even more the case in quantum physics, especially in scattering processes, where most of observable quantities in the continuum, such as the thermophysical and transport properties of gases, results indirectly from scattering phase shifts which are unmeasurable quantities themselves. Owing to their huge importance, scattering processes by van der Waals pairs have repeatedly been revisited over the last two decades, permitting nowadays by means of high-accuracy interaction potentials to account for the ever-growing sophistication of the experiments. However, there are still some unexpected features regarding the determination of scattering phase shifts in the continuum. Although approaches already exist for quantum-mechanical scattering phase-shift calculations, these methods only give a relative definition due to the arbitrariness of the arctan function. This property, although subtle at a first glance, is rather fundamental and crucial since the need for absolute scattering phase-shift calculations is mandatory when second Virial or acoustic Virial coefficients have to be determined.

In this context, we have put forward a novel formula intended for absolute scattering phase-shift calculations and we show how our formula can tackle situations involving van der Waals interaction potentials. The formula relies on Lippmann-Schwinger or Volterra equations and phase-functions concepts and permits to definitely close the problem of the arbitrariness of the arctan function.



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AEOLIAN TRANSPORT OVER WET SAND BEDS

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Aeolian transport is of great environmental importance. Environmental issues include desertification in arid regions, soil erosion in coastal areas or drifted snow in highways in snow regions. Saltation is identified as the primary mode of particle transport and characterised by two phases: (i) From a wind speed threshold, particles are entrained into the air and move into ballistic hopping. (ii) When the particles return to the ground, saltating grains bounce off the bed and can eject other particles. The amount of transported particles increases progressively as a function of the length of the particle bed subject to erosion up to a length-scale. Beyond this saturation length, there is an equilibrium state between erosion and deposition process. The wind reaches its maximum capacity of transportation and the particles flux its saturated value. Then, if the wind speed decreases, saltation will cease at a wind speed threshold defined as the dynamic threshold, lower than the static threshold. For spherical, dry and non-cohesive sand, the physics of aeolian transport is quite well understood [1]. In contrast, much less is known about aeolian transport over cohesive particle beds. Although moisture effects have been the focus of numerous studies [2], there exist significant discrepancies in experimental or model predictions and reliable and quantitative results for aeolian sand transport in moist environments are lacking.

We study the influence of the cohesion in the aeolian transport. We conducted well-controlled wind tunnel experiments with wet sand beds ranging from 0.5 to 4% of moisture content at different wind speeds. The experimental challenge is to control the homogeneity of the sand-water mixture and to minimize water evaporation during the experiments. To this end, the mixture of a 0.2mm natural sand and water was achieved in a concrete mixer and then left in a sealed container over 24 hours before it is spread evenly over the whole 7m length of the tunnel. Importantly, the air entering the tunnel is fully saturated of water vapor with the help of ultrasonic fog makers.

We investigate two different configurations of transport: (i) the first one with zero upwind particle flux and (ii) the second with a finite upwind flux. The first configuration allows us to assess the static threshold of transport while the second one provides information about the dynamic threshold. For each experiment which typically lasts one or two minutes, the mass flow rate is obtained both via sand trap measurements and particle imaging.

Results confirm that the presence of moisture within the bed increases the static threshold of transport but by a much greater factor than previously reported in the literature. For example with 3% moisture content, we found a threshold wind speed of 20m/s compared to the 8m/s given in the literature (see Fig. 1a). In contrast, the dynamic threshold is significantly lower and is close to that obtained for dry sand. Additionally, experiments with a finite upwind mass flux lead to mass flow rates comparable with those obtained for dry sand. At moderate wind speed (5.5 m/s), the mass flow rate over 3% wet sand bed is surprisingly equivalent to that found for dry sand while at higher wind speed (over 7.5 m/s), it is smaller (see Fig. 1b). These results suggest that the saturated value of transport over a wet sand bed is the same as over dry sand but that the saturation length is much longer than that in dry conditions. We strongly suspect that with a longer tunnel, the mass flow rate would have reached the same value as for dry sand at any speed. These new results clearly rise the issues of saturated state of transport over wet sand beds and the sensitivity of the saturation length to moisture content.

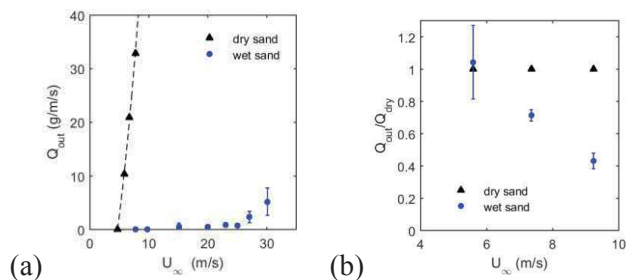


Figure 1. Transport features over a 3% wet sand bed: a) Without upwind particle flux: Downwind mass flow rate versus wind speed; (b) With upwind particle flux ($Q_{upwind}=5.6$ g/m.s): Downwind mass flow rate rescaled by the corresponding dry flux versus the wind speed.

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Study of the Welding Phenomenon in Contactors for Aeronautical Application

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Abstract:

Traveling to spend holidays somewhere, for business or even for hospitalization, can be done pleasantly by plane. According to statistics, shown by flightradar24.com, the number of flights can go up to 210000 flights per day (Figure 1).

In order to improve the performance of aircraft, to ensure travel in the best conditions, aircraft manufacturers are working on the electrification of various components to achieve more efficiency and easier aircraft maintenance. Contactors are components that have a major role in an aircraft electrical network, indeed, they must ensure the provision of significant power. When closed, the electrical contacts of a contactor allow the passage of an electrical current. An electrical arc may precede this operation, and cause a soldering of the electrical contacts. This phenomenon can lead to a malfunction or destruction of the contactors.

The purpose of my work is to build a test bench that simulates the behavior of the contactor, to control the conditions of the closing of the contacts. It will allow to test several contact materials and to study their behavior in front of the welding phenomenon, without having to manufacture and test many contactors, and also study the bounce arc during the contacts closure. For doing this study, several analyzes will be fulfilled: electrical measurements (voltage, current, power, energy, radiation, during the arc, contact resistance), physical measurements, partly in large instruments (spectroscopy, rapid imaging, technical SAXS), mechanical (contact force, welding), chemical (SEM surface analysis, EDX, nuclear microprobe, ...).



Figure 1: Number of flights per day

INFLUENCE OF CRYSTALLINE PHASES ON OPTICAL CHARACTERISTICS OF A GLASS-CERAMIC IN THE VISIBLE RANGE

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Since 1958, opal glass has been one of Arc France most popular manufactured product. Such a compound is obtained by melting a mixture of precursors through a cold-top furnace at approximately 1500 °C. Then, from a casting at about 1100 °C, forming machines give the shape to the glass articles that are subsequently quenched in air to achieve specific properties. The resulting glass-ceramics are characterized by a milky white color and exhibit a remarkable mechanical resistance. These opal glasses consist of a glassy matrix built upon silicon dioxide network containing crystalline fluoride phases (about 10 wt%). As reported in the literature, the presence of such well crystallized compounds causes the glass opalization^{1,2}. Few parameters such as refractive index, concentration, size and dispersion of the colorless crystalline particles strongly impact the overall color rendering. The desired control of all these parameters during the manufacturing process can be intricate but the impact of the aforementioned variables can be modeled via the 4-Flux method^{3,4}. Then, as shown in Figure 1, transmitted and reflected, scattered and specular fluxes can be calculated and the impact of each of these parameters determined. The color of these glass-ceramics will be discussed based on this model through the correlation between simulation and observation. The role of the crystalline part nature will be specially highlighted.

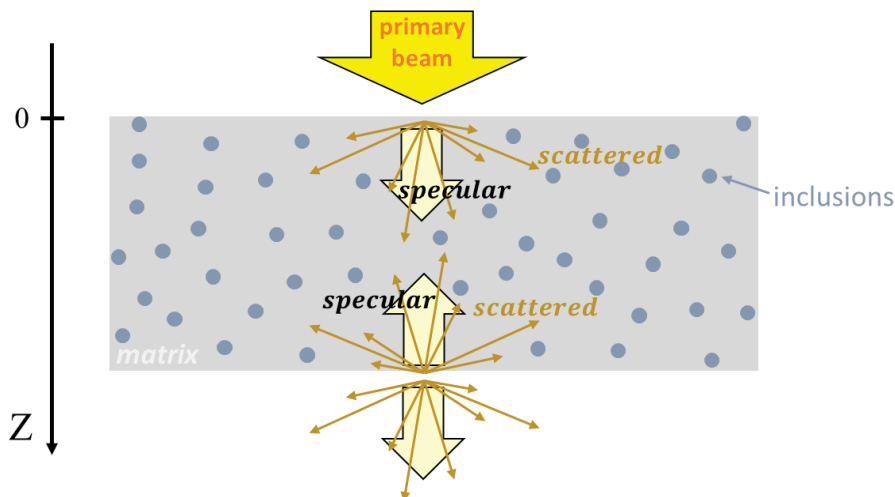


Figure 1: Determination of specular and scattered fluxes by the 4-flux method into the inclusion-matrix-type layer

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LUMINESCENT MECHANOCROMIC COPPER IODIDE CLUSTERS

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The ability to control and modify the emission properties of luminescent materials under the effect of external stress is an important feature for the development of multifunctional materials with applications as detection systems, for example [1], [2]. The development of such materials requires a good understanding of the mechanisms involved in luminescence changes. We have studied the photophysical properties of molecular clusters of copper(I) iodide for several years and we have demonstrated the sensitivity of their emission to different stimuli such as temperature (thermochromism) [3] or pressure (mechanochromism) [4], [5].



Figure 1. Luminescence mechanochromism of a $[\text{Cu}_4\text{I}_4\text{L}_4]$ (L = phosphine ligand) cluster.

We will present the luminescence mechanochromic properties of new copper(I) iodide clusters with general formula $[\text{Cu}_4\text{I}_4\text{L}_4]$ (L = phosphine ligand). These compounds exhibit a significant and reversible change of their solid-state emission when they are subjected to a mechanical stress such as grinding, as shown in Figure 1. A change in the luminescence thermochromic properties is also observed under the effect of grinding. Comparative studies of different polymorphic forms of these clusters are carried out to establish correlations between the molecular structure and the emission properties in order to improve the understanding of the mechanochromism mechanism.

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- 47 **OH Kiseok** *Silicon photoelectrodes partially coated with nickel*
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- 53 **RENAULT Louise** *Polysaccharides as innovative renewable raw materials for the development of green/blue surfactants*
- 54 **RINCON MEJIA Carlos Andres** *Prediction of odor concentration (OC) based on odor activities values (OAV) for emissions from composting*
- 55 **ROCTON Nicolas** *Synthesis of nano bioactive glass via the emulsion process for use in the biomedical field*
- 56 **ROQUET Vincent** *Fire resistance improvement of plasterboard by reflection of thermal radiations*

- 57 **ROUEINDEJI Hanieh** *Preparation of calcium complexes stabilized by C-F secondary interactions*
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- 66 **WANG Jinzeng** *Synthesis and characterization of coordination polymers: probing photo-physical properties*
- 67 **YAO Haiyun** *Synthesis; structure and luminescent properties of new hexa-lanthanide compounds based on hexa-nuclear oxo-hydroxo rare earth entities*
- 68 **ZHANG Wei** *Electrochemical processes coupled to a biological treatment for the removal of iodinated compounds*
- 69 **ZHOU Ying** *Elaboration and characterization of Ti-based superelastic films*

HETERO-LANTHANIDE COORDINATION POLYMERS BASED ON BORONIC ACID: OPTICAL PROPERTIES FOR POTENTIAL APPLICATION.

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The development of solid state light emitting materials has attracted a lot of interest for more than a decade, because of their potential application in many fields such as medical imaging, fight against counterfeiting, optical probes and temperature measurements. The ligand in the hybrid material plays an important role in the transfer of energy to the emitting metal center and, consequently, in the optical properties. Some years ago, 4-carboxyphenyl boronic acid was used as ligand for the first time by our group for studying its influence on the properties of lanthanide-based coordination polymer¹. Two crystal structures were solved and the optical properties of the homo- nuclear coordination polymers based on Tb³⁺ and Eu³⁺ were studied. Recently, isostructural heteronuclear compounds (molecular alloys and core-shell) were synthesized. Their characterization and photo-physical properties will be presented in this presentation.

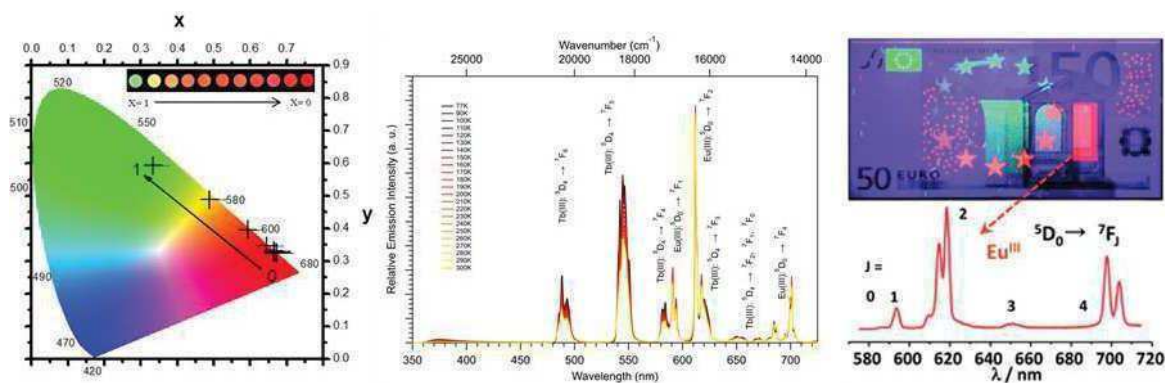


Figure 1: (left) Colorimetric coordinates for $[\text{Tb}_x\text{Eu}_{1-x}(\text{cpbOH})(\text{H}_2\text{O})_2 \cdot (\text{cpb})]_\infty$. (inset) Pictures corresponding to the pellets of the series of $[\text{Tb}_x\text{Eu}_{1-x}(\text{cpbOH})(\text{H}_2\text{O})_2 \cdot (\text{cpb})]_\infty$ under UV irradiation (312 nm) and (middle) Emission spectra of $[\text{Gd}_{0.2}\text{Tb}_{0.7}\text{Eu}_{0.1}(\text{cpbOH})(\text{H}_2\text{O})_2 \cdot (\text{cpb})]_\infty$ versus temperature (right) Europium used as taggant for anti-counterfeiting.²

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MULTIVALENT INHIBITORS OF SIALIDASES

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In recent years much effort has been devoted to the design of potent and selective glycosidase inhibitors. However, potential candidates often have a lack of selectivity and non-specific inhibition leads to side-effects. Limiting selectivity problems due to the unwanted inhibition of certain glycosidases is therefore a challenge unmet with the first generation of inhibitors.

We developed an alternative approach to the “lock and key concept” to try to achieve high affinities and selectivities for carbohydrate-processing enzymes, with a focus on sialidases.

Sialidases are involved in many physiological and pathological functions. They specifically recognize and hydrolyze the osidic bond of sialic acid displayed on cellular glycans, polysaccharides, glycolipids and glycoproteins. Many viruses, bacteria and parasites produce this enzyme to cleave sialic acids from host cells and thus unmask membrane receptors to allow adhesion and invasion.

There are several classes of sialidases, some have only one catalytic site (CAT) to cut the osidic bond, while others have an additional lectinic site called CBM (Carbohydrate-Binding Module) which is an anchoring point for glycans, thus increasing the catalytic activity of the enzyme. These sialidases with CAT and CBM are common to many protozoal and pathogenic bacteria, making them very good therapeutic targets. Furthermore, human sialidases involved in important physiological functions do not express CBMs.

Here, specific multivalent compounds capable of binding to both the CAT and the CBM of a pathogenic organism have been developed. (Figure 1).

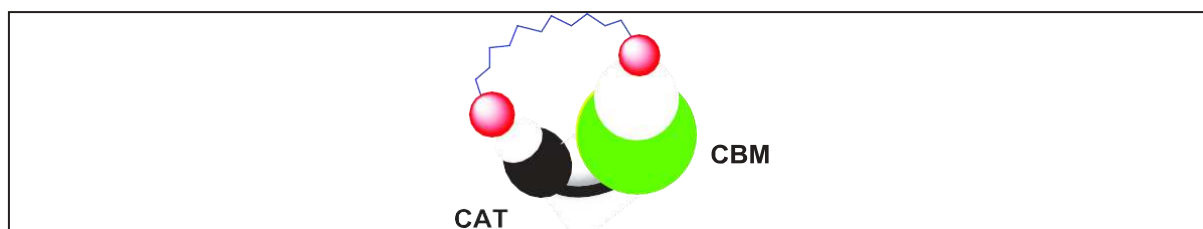


Figure 1: Multivalent homovalent CAT and CBM sialidase inhibitors

Homovalent inhibitors will be described with a single type of ligand (thiosialoside) on different structures. The structures studied are ethylene glycols (EGs), cyclodextrins (CD) and a polymeric compound (Figure 2).

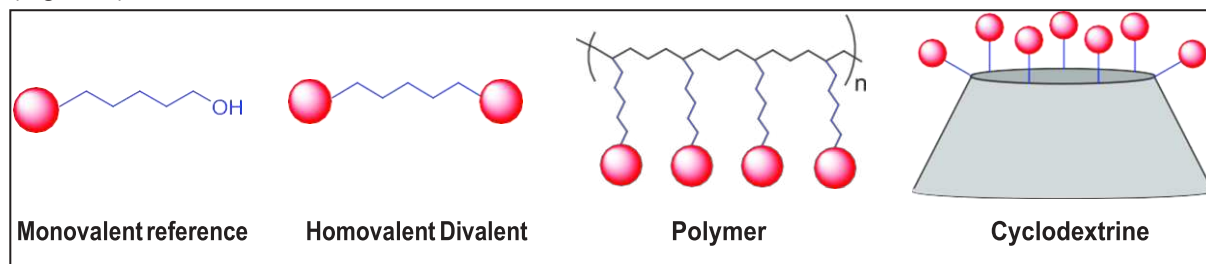


Figure 2: Multivalent structures

Several enzymes were produced with and without the lectinic domain, to determine the importance of dual targeting and the validity of the concept. Inhibition tests of the multivalent compounds against bacterial, parasitic and fungal sialidases showed inhibitory activity up to the nanomolar range.

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SELF-ASSEMBLED, TUNABLE PORPHYRIN MATERIALS

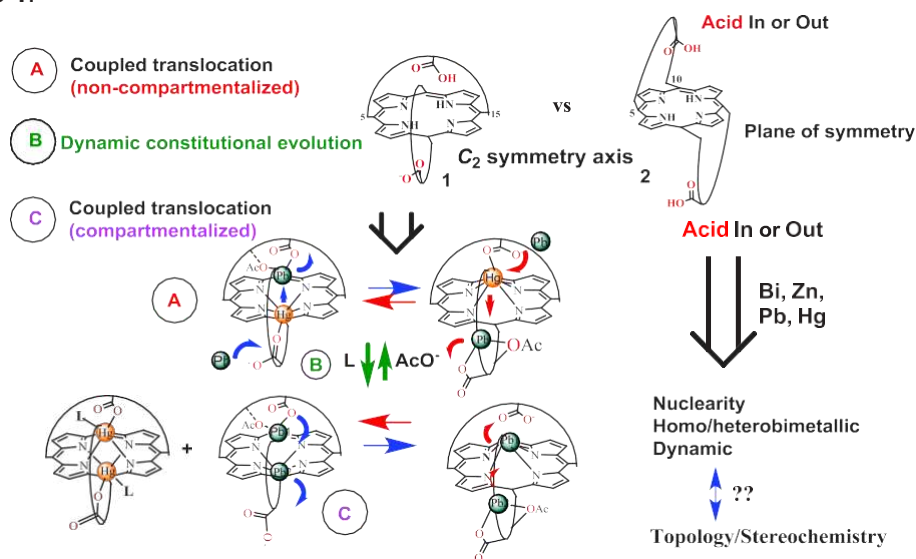
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Supramolecular coordination chemistry has been studied significantly for the construction of nanoscale objects and devices, taking profit of the lability and directionality of coordination links - and more generally of the richness of transition-metal chemistry - to control specific topologies and functions.^[1-3] A particular interest has been given to the design of molecular ligands able to stabilize a metal ion at different metal sites in a switchable manner.^[4] Among important developments, our group has previously reported a 5,15 bis-strapped porphyrin ligand **1** with an overhanging carboxylic acid group on each side of the macrocycle, and the formation of dynamic libraries of bimetallic complexes.^[5,6] These complexes exhibit coupled translocation processes, either compartmentalized **C** or non-compartmentalized **A**, tuned by dynamic constitutional evolution of the library. In order to extend this supramolecular coordination chemistry, we now report 5,10 bis-strapped porphyrin ligand **2**, which generates different isomers (in vs out) depending on the position of the carboxylate group. Coordination of **2** with different metal ions such as Zn(II), Bi(III), Hg(II) and Pb(II) has been investigated and compared to **1**.



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FLUORESCENT ANALOGUE OF THE GLYCO-GLYCERO LIPID OHMLINE, A POTENTIAL ANTIMETASTATIC AGENT.

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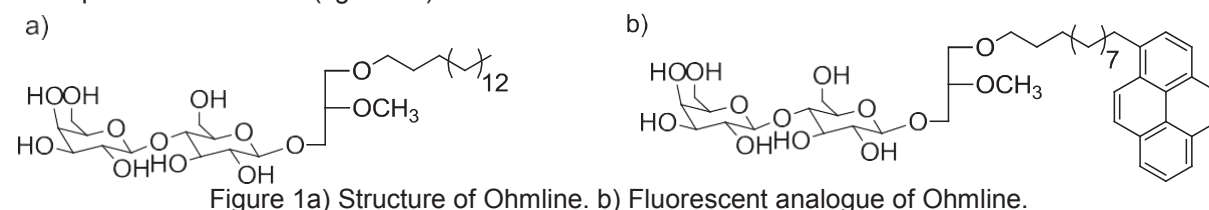
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SK3 channels, a small conductance activated potassium channels which are activated by low intracellular calcium concentration, are expressed in several cancer cell lines (breast cancer cells, human metastatic melanoma cell lines). Previous studies have shown that SK3 channels are involved in cancer cell migration and are expressed in cancer cell lines known for their invasive properties¹. Thus, SK3 channel represents a potential target for a new class of anticancer agents that would reduce cancer cell migration and potentially, metastasis formation.

Ohmline was the first efficient and non-toxic SK3 inhibitor that exhibits an amphiphilic structure (figure 1a)^{2,3}. This compound is quite selective since it strongly inhibits SK3 channels whereas SK1 is weakly inhibited and SK2 or BKCa are not modulated with this compound. *In vivo* experiments, carried out on a metastatic breast cancer murine model, have shown that the administration of Ohmline eliminated the occurrence of bone metastasis and reduced by 50% the occurrence of lung metastases⁴. These outstanding results still need to be better understood. If Ohmline is likely incorporated in the plasma membrane, its localization at a cellular scale still needs to be assessed.

With this view in mind, we report herein the synthesis of a fluorescent analogue of Ohmline. We have chosen pyrene as fluorescent moiety and this fluorescent probe was placed at the extremity of the lipid chain present in Ohmline (figure 1b).



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PHTHALOCYANINE CORED DENDRIMERS FOR PDT

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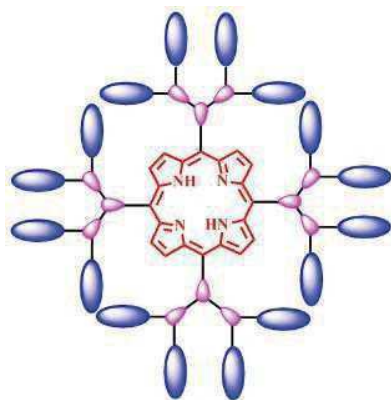
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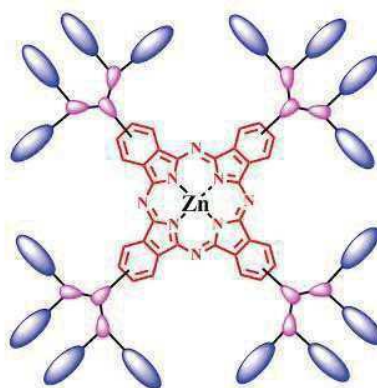
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In a previous work, we have reported the synthesis of porphyrin possessing four fluorenyl arms **TFP**.^[1-3] Surprisingly, **TFP** exhibited a remarkably high quantum yield (24%), compared to the reference tetraphenylporphyrin (**TPP**) demonstrating the capacity of the fluorenyl units to enhance quantum yields. Then, to exploit this capacity, a series of porphyrin dendrimers bearing fluorenyl dendrons was prepared.

Very recently, a series of phthalocyanines Dendrimers containing fluorenyl antennae, have been synthesized and characterized. Following our interest for porphyrin dendrimers bearing fluorenyl dendrons we wondered about changing the acceptor core macrocycle porphyrin to phthalocyanine and we studied the effect on optical properties. So, a new series of conjugated **Phthalocyanines Dendrimers** possessing fluorenyl arms was prepared and studied; It was found that these compounds emit intense red light exhibiting high luminescence and show interesting third order NLO properties. The positive role of phthalocyanine ring over porphyrin on the optical properties as well as two-photon absorption (2PA) cross-sections is clearly evidenced.



Porphyrin dendrimer G2



Phthalocyanine dendrimer G2

Key words: phthalocyanine, porphyrin, fluorenyl, dendrimers, red emission, energy transfer, NLO, PDT

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TOWARD NEW CHIRAL CAPPED LIGANDS : HEXAPHYRIN-CYCLODEXTRIN METALLO-RECEPTORS

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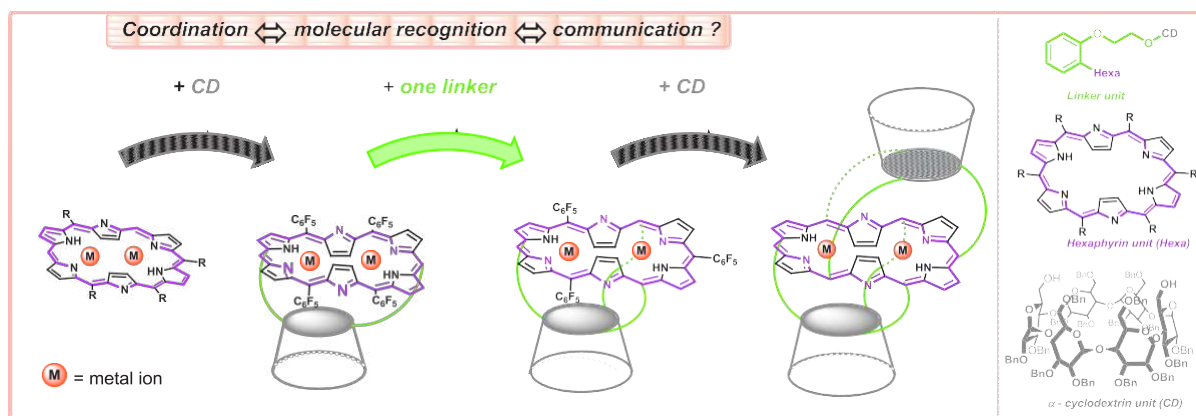
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Expanded porphyrins are macrocyclic compounds with more than 4 pyrrole rings offering several applications such as anion binding agents, photosensitizers for photodynamic therapy, contrasting agents and material for nonlinear optical applications. Hexaphyrins [1] (6 pyrrole rings) present different types of aromaticity and topology at the origin of remarkable coordination properties.[2] Whereas metallation of planar and twisted hexaphyrins has been performed successfully, it has been, so far, mostly described on « free » macrocycles (deprived of fonctionnal groups).

In our lab, we thus explore the coordination properties of capped hexaphyrins.[3] In particular, we aim to build hybrid ligands that covalently link an hexaphyrin to a cyclodextrin cavity. In these hybrids, the hexaphyrin part is either singly or doubly capped by one or two cyclodextrins, with up to 6 linkages. (Scheme 1) The hydrophobic cavity is expected to play different roles : at the level of (i) the coordination of metal ions, (ii) substrate recognition [3a-c] and, (iii) communication between substrates and metal ions. Ultimately, these hybrid ligands would lead to allosteric receptors and catalysts,[4-5] which is the concern of our researches.



Scheme 1 : Representation of the hybrid ligands

Acknowledgments : We are grateful to the Agence Nationale de la Recherche for financial support (ANR-16-CE07-0014).

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Copper free click chemistry for the development of new dye sensitized photoelectrocatalytic solar cells for the production of solar fuel Yousra BENTOUNSI^{*}, Dr Stéphane DIRING, Dr Fabrice ODOBEL

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With the increasing global energy demand and the depletion of fossil fuels, the conversion and storage of solar energy into chemical potentials have become one of the main challenges of today's chemistry. Hybrid nanomaterials consisting of a nanocrystalline metal oxide film whose surface area is coated with molecular system have considerable implications for the development of dye sensitized photoelectrochemical cells (DSPECs) [1] for the conversion of solar energy into chemical fuels (H₂, CO, methanol,...) (figure1).

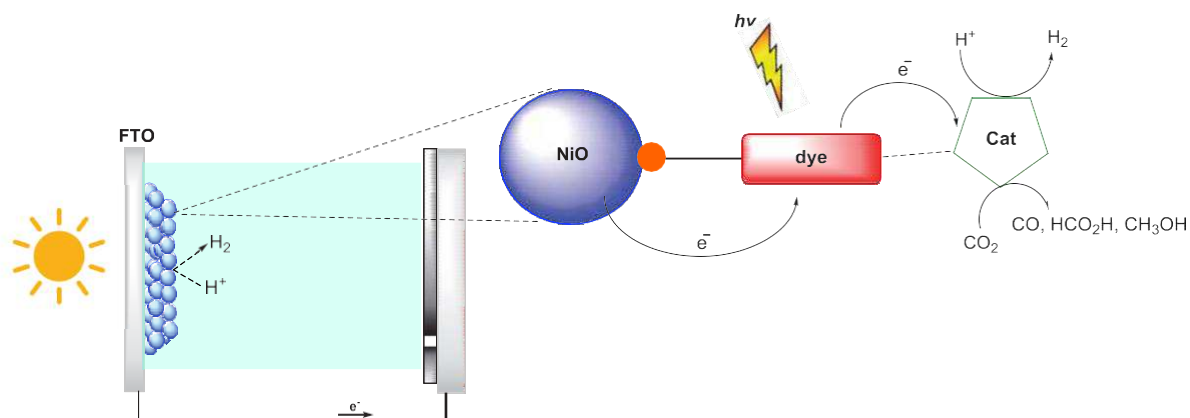


Figure 1: Working principle DSPECs

In this study, we have designed and synthesised a new DSPECs devices, based on a "click-chemistry" reaction that has been developed recently in the laboratory. This reaction is based on a Huisgen reaction by thermal activation between a crosslinking agent substituted with alkyne functional groups and a sensitizer initially grafted onto the surface of a semiconductor oxide and substituted with azide functions (figure2). Through this work, we will functionalize dyes, initially grafted on the surfaces of mesoporous films based on NiO and TiO₂[2], by organic molecules or by coordination complexes that can act as secondary electron acceptors, catalysts or light-collecting antennas to develop more stable and efficient photoelectrochemical hybrid systems to activate protons and carbon dioxide into chemical fuels.

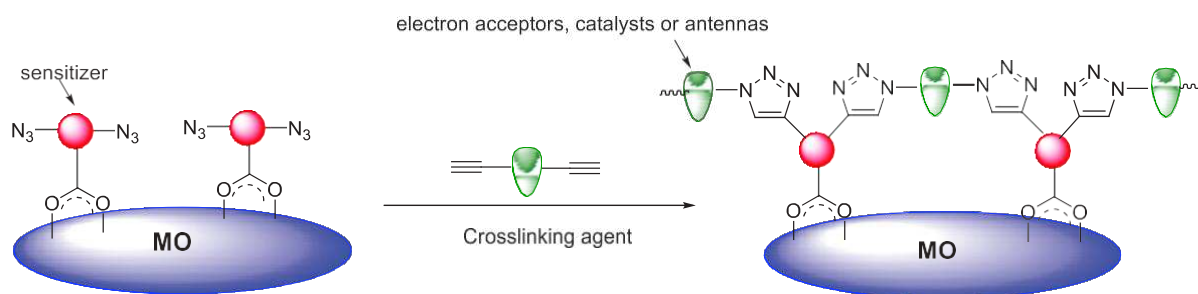


Figure 2: Schematic representation of click chemistry reaction for the functionalization of mesoporous metal oxide (MO)

¹ Brennaman, M. K.; Dillon, R. J.; Alibebaei, L.; Gish, M. K.; Dares, C. J.; Ashford, D. L.; House, R. L.; Meyer, G. J.; Papanikolas, J. M.; Meyer, T. J.; J. Am. Chem. Soc, 2016, **138**, 13085-13102.

² Odobel, F.; Pellegrin Y.; J. Phys. Chem. Lett., 2013, **4**, 2551-2564.

COATED CURRENT COLLECTORS FOR HIGH VOLTAGE LITHIUM ION BATTERIES

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The way of live of current society requires a lot of energy due to the use of electronic mobile devices such as smartphone or laptop and the development of electric vehicle. The growing need for electrical energy storage systems leads industrials to always work on improving lithium-ion batteries performances. These batteries are composed of two electrodes coated on a current collector and separated by an electrolyte. A way to increase energy and power densities of such system is to increase their output voltage. For this purpose, many studies have been focused on the development of new high-voltage cathode material (working potential $> 4,2$ V vs Li^+/Li). However, although promising materials have been found (nickel-rich and lithium rich layered oxides, high voltage spinel oxides and high voltage polyanionic compounds) their practical use is actually hindered by the degradation of the electrolyte and other cell components [1]. Especially, positive current collector (traditionally an aluminium foil) undergoes severe oxidation at these high potentials [2]. One approach to prevent aluminium oxidation is to use a protective coating [3]. ARMOR designs and produces in recent years coated current collectors and wants to expand its range of product to propose performing current collector for high voltage applications. In this work we present the anodic behaviour of aluminium current collector in various electrolytes and the ability of ARMOR coatings to protect current collector from oxidation.

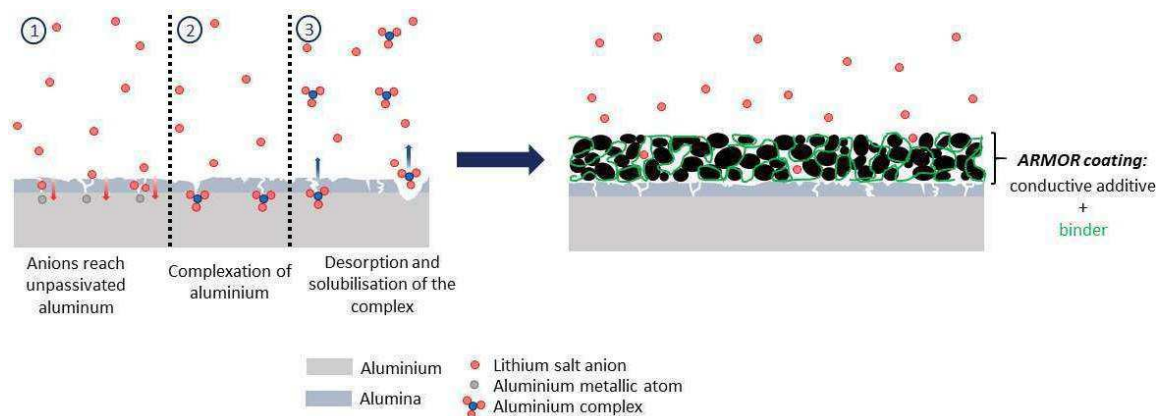


Figure 1: Protection of aluminium current collector from anodic dissolution by a protective coating

References

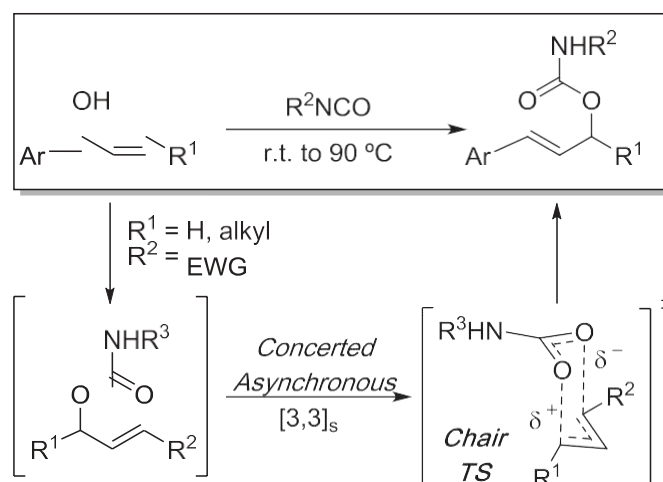
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[3,3]-SIGMATROPIC OXO-REARRANGEMENT OF ARYL SUBSTITUTED ALLYLIC CARBAMATES

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[3,3]-sigmatropic rearrangements have long been used in organic chemistry due to the fact that they allow regio- and stereoselective carbon-carbon or carbon-heteroatom bond formation with relative ease. Among the carbon-oxygen bond forming reactions, the sigmatropic oxo-rearrangement of allylic carbamate is not highly investigated. In fact, the scarce examples described in literature require using metal-catalysed methods based on palladium or mercury salts.¹ However an unexpected [3,3]-sigmatropic oxo-rearrangement occurred when we tried to investigate an allyl cyanate/isocyanate rearrangement on aryl substituted allylic carbamates.



Thus, several linear allyl carbamates were prepared via a “one-pot” process starting from allylic alcohols. The rate of the rearrangement is highly dependent on the electron density of the aryl ring and on the nature of isocyanate used.

The molecules bearing a carbamate group play an important role as synthetic intermediates as well as in modern drug discovery and medicinal chemistry.² Therefore we decided to further explore the substrate scope and to try to overcome the limitations of the process through a microwave-assisted method. In fact this latter has become a popular theme in organic chemistry. Microwave heating has turned out to be a very efficient method to reduce reactions time and to increase products yields. Thus, the use of this technology has become a very useful tool for the medicinal chemistry community for whom reaction speed play a crucial role for drug discovery.³

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MULTISCALE NMR ANALYSIS OF ENTIRE MICROALGAE CELLS TOWARDS IN-VIVO PROFILING OF LIPIDS

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Microalgae are microscopic unicellular photosynthetic organisms proposing highly uncharacterized chemodiversity and a great ability to produce valuable sustainable products. They are used in a wide range of applications, from fish farming to the production of specific compounds such as pigments or bioactive products. Only a minor proportion of the millions of species spread in the environment are currently investigated, constituting therefore a high potential research subject.

However, the characterization of the microalgae intracellular compounds often requires one or several extraction step(s) associated with diverse analytical techniques that provide insights on its compositional information. The complexity of the matrix and of its chemical diversity constitutes a strong bottleneck often limiting its deep chemical characterization.

In this context, we propose to assess the potential of Nuclear Magnetic Resonance (NMR) for the profiling of the microalgae lipids. As biological model, we have investigated *Parachlorella kessleri*, a microalgae known to accumulate large quantity of lipids (up to 40 % of dry weight) under specific cultural conditions [1]. This preliminary investigation was carried out on different samples (extracts or entire cells) and at different magnetic fields: High Field (HF) NMR which provides the best sensitivity and resolution, but also Low Field (LF) NMR which has strong potential for the online analysis of microalgae lipids. Indeed, recent improvements in LF NMR pulse sequences, especially in solvent suppression [2] and Ultra Fast (UF) NMR [3] have pushed the limits of LF NMR, thanks to the addition of a gradient coil in the spectrometer.

We present here the results we have obtained on the evolution of the lipidic NMR profiles acquired on extracts and on entire cells. This will constitute the first step to assess the potential and the limitations of NMR to monitor in vivo lipid accumulation. In the next future we will focus our efforts on the quantification of the different lipid classes and other relevant compounds, both with HF and LF NMR.

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NARROW LINEWIDTH InP/Si₃N₄ LASER FOR LIDAR APPLICATIONS

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LIDAR (Light Detection And Ranging) systems are becoming very popular thanks to a growing number of applications such as 3D imaging for autonomous vehicles and robots, remote gas concentration sensing or wind measurements. A high power compact tunable laser source with a narrow linewidth is required to achieve the best performances. But, these specifications are difficult to gather in standard laser sources. That's why we intend to develop an original external cavity laser architecture (fig. 1a) [1] which combines two types of materials: a Reflective Semiconductor Optical Amplifier (RSOA) made of InGaAsP/InP with an optical passive chip on silicon substrate containing a Bragg reflector.

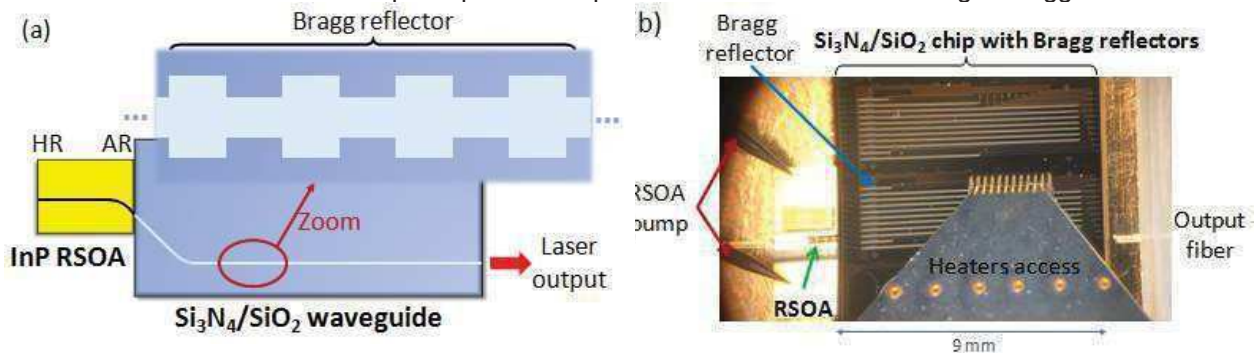


Fig. 1 : (a) Hybrid laser cavity structure, the passive circuit is a waveguide containing a Bragg reflector formed by a controlled indentation of the wave guide. (b) Picture of direct butt coupling between a RSOA and a chip containing Bragg reflectors surmounted by heaters.

The 1 mm-long RSOA is based on an asymmetric semi-insulated buried heterostructure. It provides the gain of the hybrid laser cavity and forms the back mirror of the cavity thanks to the High Reflection (HR) coating on one side, the other side being AR-coated (antireflection). In the passive chip, the 9mm-long silicon nitride waveguide contains a Bragg reflector, in charge of closing the laser cavity and selecting one longitudinal mode. The direct butt coupling of these components has been done successfully (fig. 1b), leading to a compact laser.

We obtained an optical output power of 10 mW, and a threshold around 65 mA. Moreover, the hybrid laser complies with LIDAR specifications since it exhibits a side mode suppression ratio of 60 dB. Finally, thanks to a delayed self-heterodyne workbench, we measured an optical linewidth ranging from 20 kHz to 60 kHz, depending on the quality of the coupling between the RSOA and the Bragg reflector. Such small linewidths demonstrate the spectral qualities of the device. Furthermore, by improving the quality of the passive cavity, we even expect an improvement of the linewidth for the next generation of hybrid laser.

The tunability of the laser has been obtained by changing the bias current of the RSOA on one hand, and by controlling the temperature of the passive waveguide thanks heaters placed over the Bragg mirror on the other hand. Changing the bias current heats the RSOA and increases the length of the cavity, thus shifting continuously the position of longitudinal modes. Whereas, heating the Bragg reflector will affect the reflected Bragg wavelength, thus the position of the Bragg filter can be controlled, and permits to select different longitudinal mode.

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Acknowledgments:

This work has been achieved with the support of the Direction Générale pour l'Armement (DGA) and of the Agence Nationale de la Recherche Technologie.

MACHINE LEARNING APPLIED TO CASTING PROCESS CONTROL BY INTELLIGENT IDENTIFICATION OF CASTING DEFECTS AND 3D RECONSTRUCTION IN LEAD ALLOYS PARTS

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Background

Lead parts are used every day in nuclear industry to protect salaries from radiation. Due to the high density of lead alloys, 3D mapping of internal casting defects in lead parts is slightly difficult. Tomography and other nondestructive testing methods which are widely used for metal alloys observation are, in this case, extremely limited by the thickness of parts, give low resolution and require high-energy sources. A more economical method based on simple devices, open and free software programs linked to machine learning algorithms allows small and medium size businesses an understanding of their means of production with an intelligent recognition, segmentation and 3D reconstruction of internal casting defects and a statistical modeling of their production parameters.

Method

The method consists in machining the parts with a fine cut depth value. Each machined surface is photographed by a camera with a suitable lens to avoid distortion of final images. After a brief transformation of images stack, investigated casting defects are identified and segmented with the Machine Learning program "Weka" developed by Wekato University included in Fiji open software. An assembly of the slices allows a 3D reconstruction of the object. Its analysis enables the quantification of the defects such as surface porosity ratio, the number of porosity particles, and position of shrinkage... The effect of each process parameter on defects is quantified with fractional factorial design of experiment with the R open software.

Results

In the industrial case studied, this method allowed an identification and a quantification of main parameters affecting casting quality of the injected part intended for nuclear application. A 3D reconstruction enable to determine the location and the magnitude of segmented defects in function of machine parameters. The injection molding machine has been stabilised by a focus on the most critical factors. A comparison with numerical simulation results obtained with the finite element method allowed to make numerical simulation models more realistic.

Conclusion

As expected, this study not only pointed out the impact of unmolding compounds on porosity ratio and the impact of mold temperature on shrinkage defect but also gives the non-linear equations of each defect in function of machine parameters. Current developments are now going to improve the resolution of 3D reconstruction to increase the precision of calculation based on these 3D models.

Covalent functionalization of cellulose - Formation of a photoresponsive paper for optical data storage

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Cellulose is an organic compound, and more precisely a polysaccharide which represents the main part of wood, paper and cotton. Many different methods were invented to functionalize cellulose such as the use of wax or oil^[1], polymerization in solution at the surface of the cellulose^[2] or even by chemical vapor deposition^[3]. Through the grafting of single molecules under the surface of the cellulose, it could be possible to make a modification of the cellulose properties. Indeed, previous research in our laboratory at the University of Nantes has shown that the grafting of some compounds enables the modification of cellulose from a hydrophilic to a hydrophobic state, with a spatial control, by the grafting of dithiodiglycolic acid onto cellulose in a first step and then, a thiol-ene or thiol-yne reaction with hydrophobic molecules upon irradiation light at 365 nm. These reactions were optimized, and the scope was studied. Finally, these papers were analysed by elemental analysis (EA), infrared spectroscopy, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and measurement of contact angle. Such reactions could be an alternative way for the modification of cellulose in paper or textile industry.

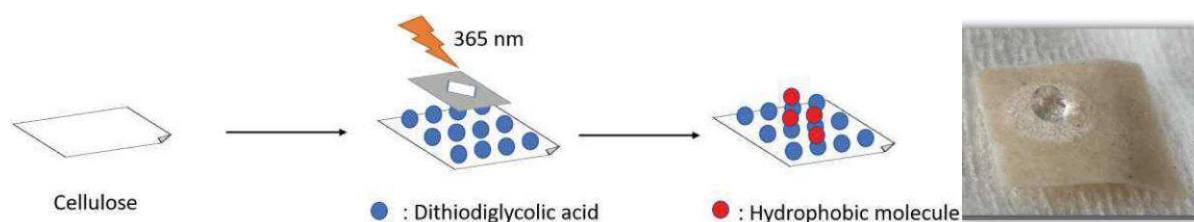


Figure 1: Formation of hydrophobic paper through thiol-ene and thiol-yne reaction

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BROADBAND EMISSION IN ZINC PHOSPHORUS OXYNITRIDE GLASSES

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Phosphate glasses have been widely used in optical devices such as laser and light emitting devices due to their high transparency, good formability, high dopant concentration, and good chemical durability[1]. On the other hand, compare to rare earth (RE)-doped glass, a typical example of an optical material containing activators, rare earth free (REF) such as ns²-type emission center doped glass has been perceived as the better phosphor for lighting due to its broader emission band determining a higher color rendering[2]. Recently, zinc phosphate glasses have been shown to be a good host for emitting centres, especially for REF centres such as Sn²⁺ and Sb³⁺[3]. However, there is very few report on the emission of the zinc phosphate glass host itself. In this report, a broadband strong emission at 420nm was observed in the zinc phosphate glasses host for the first time through replacing oxygen by nitrogen. We assign this unique blue emission to Zn²⁺: nd¹⁰-type emission center. The absorption, excitation, photoluminescence and luminescence decay spectra of the prepared samples were shown in Figure 1. The prepared glasses may be useful as colorless and transparent fluorescent materials, such as for lamps and LED lighting[4].

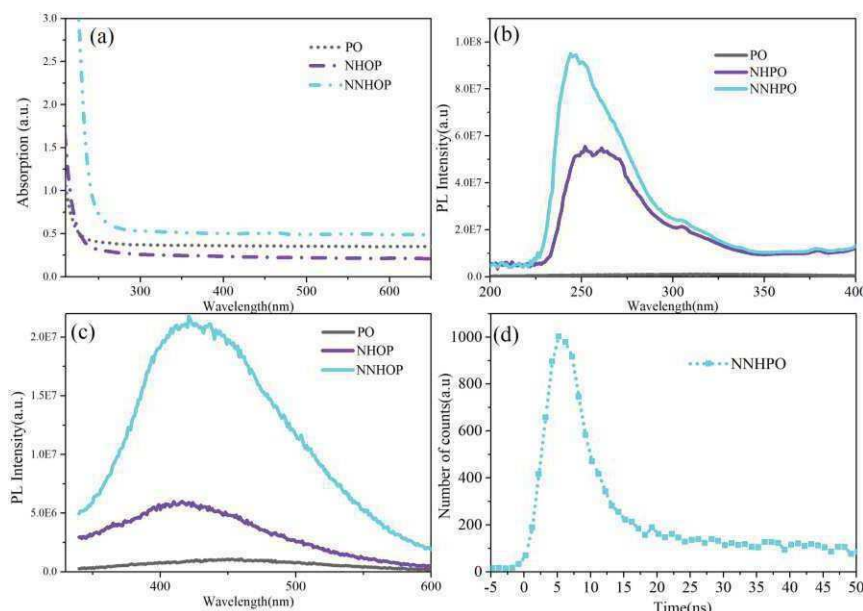


Fig 1. The asorption(a), excitation(b), photoluminescence(c) and luminescence decay(d) spectra of the prepared samples.

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Study on the structural and optical properties of InGaP/SiGe/Si

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Due to superior photoelectric properties, III-V semiconductors have been widely used for many photoelectric devices, such as LED, optical waveguide, laser and so on, which are applied to various fields in our daily life (Fig.1).

Today, integration of III-V semiconductors on Si substrate remains a very hot topic [1] which aims to combine the mature silicon-microelectronic technology with the advantages of optical data processing. GaP shows a strong advantage of low-lattice mismatch to Si and has been widely studied. However, the GaP material has an indirect bandgap and relatively low carrier mobility, which intrinsically limit its optical performances. Therefore, the pseudomorphic integration of InGaP on a relaxed SiGe/Si pseudo-substrate is expected to overcome these issues. In this work, the structural and optical properties of an InGaP/SiGe/Si sample were studied by temperature- and power- dependent photoluminescence (PL), transmission electron microscopy (TEM) (Fig.2), energy-dispersive X-ray (EDX) elemental mapping techniques and so on. One PL emission peak is proved to come from surface InP quantum dots. Other PL emission peak with a superlinear to linear power dependent behaviour is considered to result from In-rich antiphase boundaries[2], in good correlation with theoretical predictions[3].

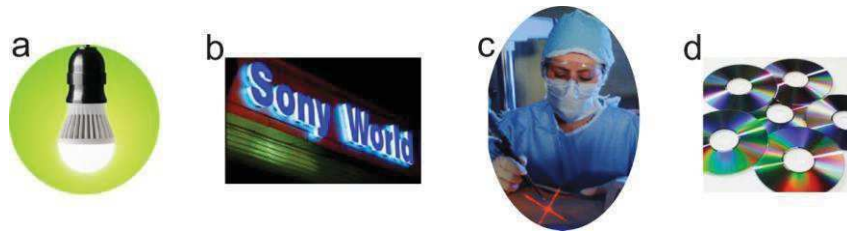


Figure 1 : The applications of III-V semiconductors in our daily life:(a) LED lighting (b) LED advertising board (c) laser surgery (d) laser discs

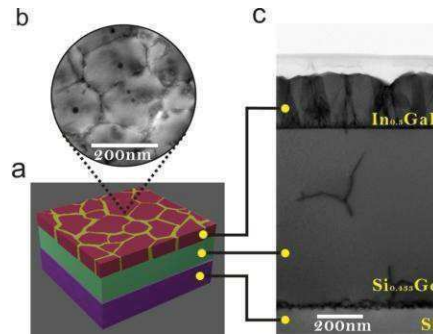


Figure 2 : Schematic(a), plan view(b) and cross-sectional view(c) TEM images of the InGaP/SiGe/Si platform

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DEVELOPMENT OF ELECTROCHEMICAL MICROSENSORS FOR THE DETECTION OF ORGANIC PESTICIDES RESIDUES AT SOLID MATERIALS

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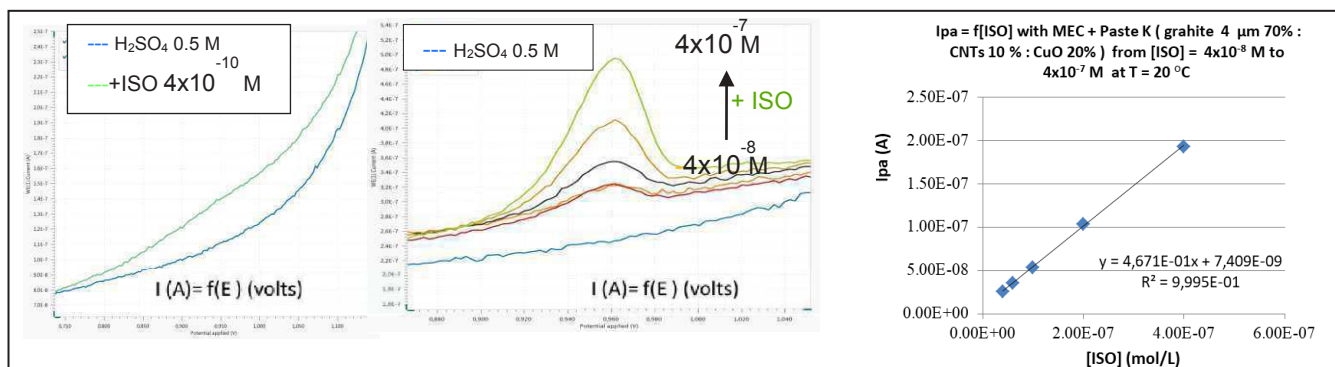
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In spite of their importance to maintain a sufficient plant production, many of the pesticides used in agriculture are long time persistent [1], and very toxic for human health (causing dangerous diseases such as disorder of the neurological and immune, fertility troubles, congenital malformations, cancers)[2]. Hence the pesticide analysis in the environment is crucial and traditionally uses the chromatographic techniques coupled with selective detectors systems. Although essential, these techniques are relatively expensive and require long time for preparation and analysis of samples [3-4].

In our project, we develop new electrochemical micro-sensors for the trace detection of targeted pesticides with nanostructured composite materials introduced in cavity microelectrode (CME) as sensing electrode. For electroactive pesticides, this strategy is an alternative to chromatographic methods due to its operation simplicity, acceptable sensitivity, wide linear concentration range, low limit of detection and quantification, possibility of miniaturization, affordable cost of instrumentation, and relatively short analysis time.

In this work, traces of Pesticides are detected with the developed micro-sensors by cyclic voltammetric techniques after an adsorption step into the composite material include in a cylindrical microcavity ($\varnothing = 50 \mu\text{m}$, $h = 17 \mu\text{m}$). Carbon pastes in the CME electrode are constituted by micro-sized graphite powders mixed with multiwalled carbon nanotubes (CNTs) and copper oxide (CuO) or by solid phase used in solid phase extraction. Now four pesticides (isoproturon (ISO), linuron (LIN) used as phenylureas herbicides, Fipronil (FIP) used as phenylpyrazoles insecticide and bentazon (BEN) used as thiadiazine herbicide have been studied. Step times for the adsorption and conditioning steps, cyclic voltammetry parameters and composition of the electrolyte have been optimized.

The best results are obtained with isoproturon (ISO) with a notable detection limit of $4 \times 10^{-10} \text{ mol.L}^{-1}$ in aqueous acid medium and $4 \times 10^{-8} \text{ mol.L}^{-1}$ in electrolyte containing acetonitrile. The calibration curves were linear from $10^{-8} \text{ mol.L}^{-1}$ to $10^{-6} \text{ mol.L}^{-1}$ and it appears that, for water samples, standard addition method is recommended to a better accuracy.



Cyclic Voltammograms in 20 mL H₂SO₄ 0.5 M at MEC ($\varnothing = 50 \mu\text{m}$, $h = 17 \mu\text{m}$) + Paste (graphite 4 μm 70% : CNTs 10% : CuO 20%)
 $v = 10 \text{ mV.s}^{-1}$; $T = 20 \text{ }^\circ\text{C}$; adsorption time = 14 min,

Actually, we detect traces of ISO in aqueous and organic solutions. We should expect the detection in vegetables samples after extraction by ACN.

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CHARGE TRANSFER AND HYDROGEN BONDS: TWO SUPRAMOLECULAR INTERACTIONS COMBINED TO FORM JANUS NANOCYLINDERS

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Janus nanoparticles are non-homogeneous colloids which possess two faces of different chemistries. Spherical Janus particles have already found applications as sensors in two-color display panels, catalysis or as emulsion stabilizers.^{[1], [2]} The construction of Janus nanocylinders still constitutes a challenge because of their small size and their 1D shape and only few strategies, based on the self-assembly of incompatible block copolymers,^{[1], [3], [4]} allowed their preparation. Recently, Catrouillet and al. attempted to prepare Janus nanocylinders via a supramolecular approach in solution, but the incompatibility of the polymer arms decorating the nanoparticles was only sufficient to lead to “patchy” particles instead of true Janus nanocylinders.^[5]

The current project proposes a new strategy to reach Janus nanocylinders regardless of the polymer incompatibility by combining two types of non-covalent interactions, i.e. 1/ hydrogen bonding (through urea groups),^{[4], [6]} and 2/ charge-transfer complexation (CTC).^[7] The concept lies in designing two complementary building blocks, bearing each a different polymer arm (P1 and P2 respectively) and able to co-assemble in solution via CTC and hydrogen bonding to form cylindrical nanostructures. Proper positioning of the hydrogen bonding units on both molecules relative respectively to the electron poor (acceptor, A) or electron rich (donor, D) units should force the segregation of the polymer arms into a Janus organization no matter their incompatibility (**Fig 1**).

This presentation will focus on the synthesis of each building block depicted on Figure 1 before presenting preliminary self-assembling studies in solution.

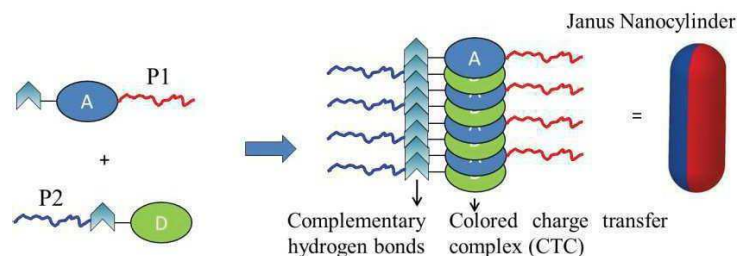


Figure 1. Forcing the formation of cylindrical Janus nanoparticles through complementary supramolecular interactions (hydrogen bonding and charge transfer complexation)

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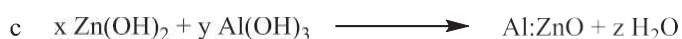
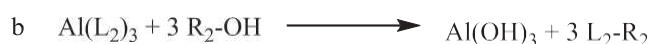
PLASMONIC NANOCRYSTALS SYNTHESIS: CONTROL OF THE MORPHOLOGY

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The synthesis and the physical properties of metallic plasmonic nanocrystals are widely described. Their interaction with the visible light is the subject of extensive studies both for fundamental research and industrial applications. Among them, transparent conductive oxides such as tin-doped indium oxide or aluminium-doped zinc oxide showed promising results in addition to their metallic plasmonic nanocrystals character [1]. Indeed, their plasmonic band is shifted to the infrared wavelengths which made it interesting for a variety of applications from solar cells to buildings thermoregulation. Herein we present the work carried out on the aluminium-doped zinc oxide nanocrystals (AZO NCs) to control the morphology of the nanocrystals and thereby tune the plasmonic band.

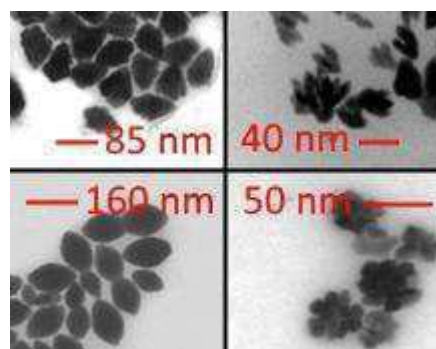
The synthesis of AZO NCs in organic media is performed at high [2]. The solution containing the alcohol initiator is injected in the solution of the metal precursors at high temperature (Scheme 1). At first, the alcohol initiator reacts with the metal precursors to get some hydroxyl function on the metal



Scheme 1 Reaction between metal precursors and initiator alcohol (a-b) condensation of two metallic precursors (c).

precursor (a and b). Then, there is a condensation reaction between two precursors resulting in the formation of nuclei (c). The size, the shape and the Al/Zn doping level of AZO NCs have been tuned. The mean parameters are the time and the temperature of the synthesis, as well as the ration between the metallic precursors and the alcohol initiator. Until now, four different shapes have been obtained and characterised by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), diffraction light scattering (DLS), scanning and transmission electron microscopy (STEM, Scheme 2), Raman spectroscopy. The effective doping level has been investigated by Graphite Furnace Atomic Absorption Spectroscopy (GF AAS) and Energy Dispersive X-Ray Spectroscopy (EDS).

Most synthesised AZO NCs present a board plasmonic band with a maximum of absorbance from 6 μm to 14 μm depending of the geometry and the doping level. Future work should allow to get smaller AZO NCs more comparable to quantum dots with a plasmonic band around a wave-length of 4 μm .



Scheme 2 TEM of obtained AZO NCs

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Acknowledgments

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IMPACT OF MODE-HOPPING NOISE ON INGAN EDGE EMITTING LASER RELATIVE INTENSITY NOISE PROPERTIES

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In this study we report through a comparative analysis of optical spectrum, L-I curve and relative intensity noise (RIN) measurement, the impact of mode hopping on the overall intensity noise dynamics of InGaN edge emitting lasers.

We show how mode clustering commonly observed in such lasers is at the origin of strong modulation of the emission spectrum. This modulation induces different spectral behaviors depending on the pump current, which all have their own noise signature. The discrepancy between the different regimes can be as high as 20 dB and is detrimental for many applications requiring high signal to noise ratio.

Our experimental setup based on Fourier transformation of the measured photocurrent allow us to deepen the study of RIN measurement through continuous noise analysis in frequency domain. Simultaneous measurements of the optical spectrum, Radio Frequency (RF) intensity noise in function of the pump current fluency give access to the rich dynamics of those lasers.

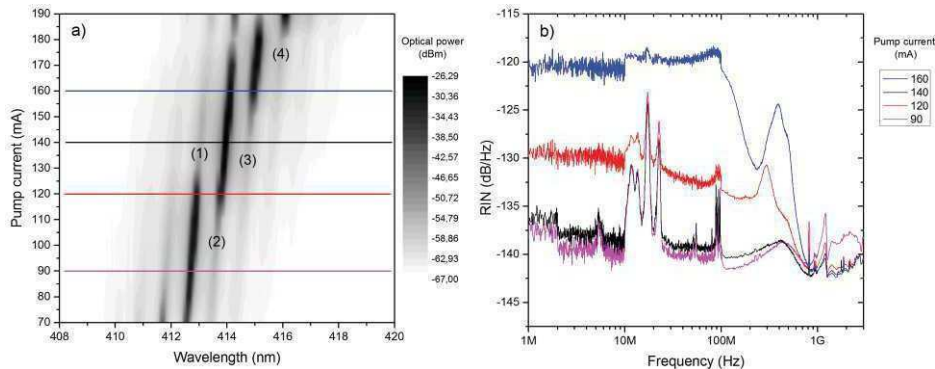


Figure 1 a) Optical spectrum evolution in function of the pump current above the laser threshold. b) RIN measurement for specific current values revealing the impact of mode hopping competition in InGaN laser.

Using a simple numerical model, we explain why the observed bimodal regime induces a dramatic RIN increase. This additional noise occurring at specific frequency ranges is detrimental for devices, which need to be frequency-modulated.

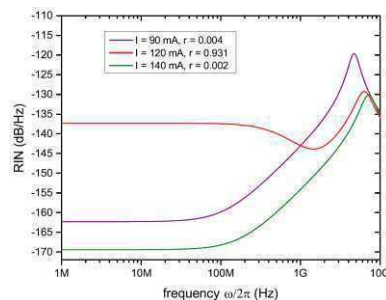


Fig. 2. Variation of the dual-mode RIN for different values of mode power ratio r .

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Degradation of flumequine in real hospital wastewater by using Fe-ZnO composite under UV-A irradiation

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Context

The removal of emerging pharmaceutical pollutants in wastewater has attracted increased attention during these last decades due to their persistence in environment and the ineffectiveness of conventional wastewater treatment systems. To overcome this, new processes called Advanced Oxidation Processes (AOPs) were investigated.

Regarding to water purification and environmental protection, photocatalysis is one of the commonly used methods among AOPs. In order to degrade pharmaceutical pollutants from low-cost materials, zinc oxide, a chemically stable and environmentally friendly material [1] have been synthesized by solvothermal method in University of Konkuk in South Korea as part of the PHC Star project.

However, one of the major problems of ZnO photocatalysis is the rapid recombination of the photogenerated electron-hole pair, which thus decreases the degradation efficiency. Some works reported that the doping of metallic or non-metallic species incorporated in photocatalysts would permit to resolve this problem because dopant-induced donor and acceptor states act as electron traps or holes resulting in better photocatalytic activity [2]. In our study, iron was used as dopant due to a possible reduction in ferrous ion, thus trapping the electrons or photogenerated holes.

Study and Results

Figure 1 exhibits the degradation efficiencies of flumequine (FLU) versus time with different weights of iron (Fig. 1A) and in real wastewater (Fig. 1B). The best performance was obtained with 0.7% wt. Fe-doped-ZnO in ultra pure water. Adding of 0.5 mM of sodium persulfate led to complete FLU degradation (Fig. 1A). For real wastewater, 0.7% wt. Fe-doped-ZnO catalyst showed a best performance compare to TiO₂ for FLU removal (Fig. 1B).

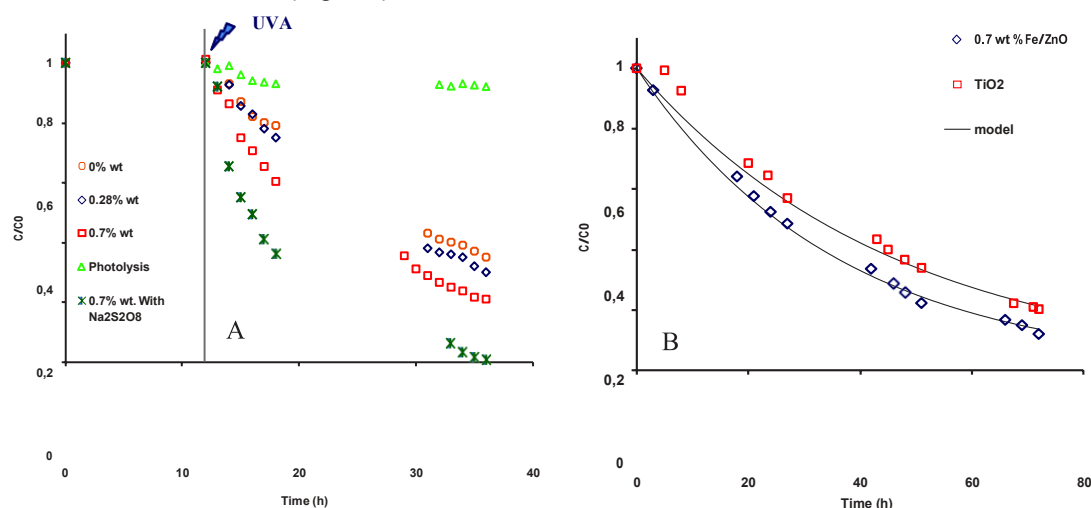


Fig.1: Flumequine degradation efficiencies under UV-A light in ultra-pure water (A) and real hospital wastewater (B). Experimental conditions: [FLU]=5 μ M, [Catalyst]=0.025 g/L, pH=7.0 \pm 0.2, UV-A light intensity = 3.4 mW/cm², feed flow rate = 3.7 mL/s, room temperature.

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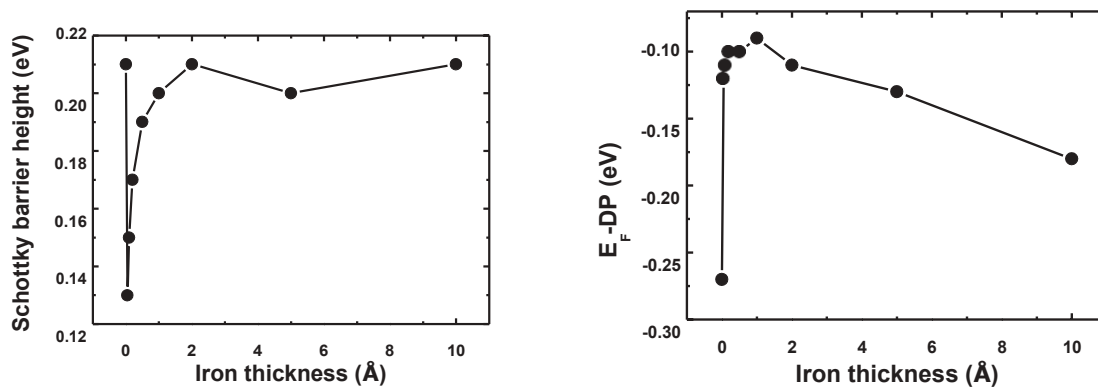
XPS as an effective method to study the band alignment in Fe/2D Solid/Silicon heterostructure

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The control of interface resistance is one of the key parameter for semiconductor based spintronic devices [1]. Despite the all development of oxide tunnel barrier, notably MgO, this control is hardly achieved with conventional oxide based barriers due to deposition-induced interface states and associated Fermi level pinning. 2D crystals (graphene, h-BN, MoS₂ ...) have therefore been seen as an alternative to design new heterostructure for improved spin injection into semiconductor [2,3]. In fact, due to the weak Van der Waals interaction between 2D solids and silicon, interface states are strongly reduced. We studied by X-ray photoemission spectroscopy (XPS) the band alignment and interface chemistry of iron (Fe)-Graphene (G)- hydrogen- passivated silicon (Si:H). We found that silicon is always close to flat band conditions, indicating that Fermi Level is unpinned on the semiconductor side of the G/Si(100):H interface. Iron deposition onto G/Si induced little band bending. This band bending is, moreover, strongly reduced compared to Fe/Si contact. We also studied the impact of iron on G and observed that the metal deposition induced doping of the latter. Moreover, as is shown the figure 1, the C1s and Si2p level movement are the same. This comportment is observed for p and n silicon for all dopant concentration.



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ORGANIC SEMI-CONDUCTORS BASED ON POLYCLIC AROMATIC HYDROCARBONS (PAHs) WITH P-CONTAINING SEVEN MEMBERED RINGS

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Polycyclic aromatic hydrocarbons (PAHs) are organic molecules featuring a bidimensional backbone composed of sp^2 -C atoms. This particular structure confers them unique properties in term of reactivity, optical/redox activity, self-assembly (through weak intermolecular π -stacking interactions) and opto-electronic device performances like OLEDs (Organic Light-Emitting Diodes), OFETs (Field Effect Transistors) and OSCs (Organic Solar Cells) [1]. They are thus an important class of organic semi-conductors. In order to modify their properties, PAHs including heteroatoms (S, N, B, P, Si) have been studied [2]. Our research group has also worked on PAHs and especially on P-containing PAHs featuring phospholes (aromatic five membered rings including a phosphorus atom) [3]. Indeed, P- derivatives have several advantages: they are stable and it is possible to tune their chemical environment as the phosphorus can be tri-, tetra- or pentavalent and they can be used as ligand for coordination complexes with transition metals.

In this project, we want to extend the family of P-containing PAHs by changing the size of the P-heterocycle. For example, we studied 7-membered P-heterocycles (phosphepines derivatives **1**, Fig 1)). The modification of the ring size will allow modifying the geometry as well as the conjugation.

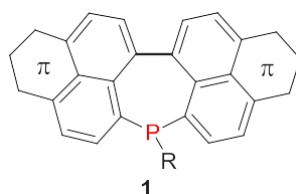


Figure 1. Target phosphepines

A whole family of phosphepine-based PAHs has been prepared (**2-5**) (Fig 2). They were fully characterized including X-ray diffraction. These compounds are luminescent in solution and in the solid state. The optical and the electrochemical properties were experimentally studied (X-ray structure, UV-vis abs/emission, cyclic voltammetry) and theoretically (DFT calculations). Due to their interesting properties these compounds appeared as potential organic semi-conductors that can be used in the future in everyday life opto-electronics devices (lightning, screens...).

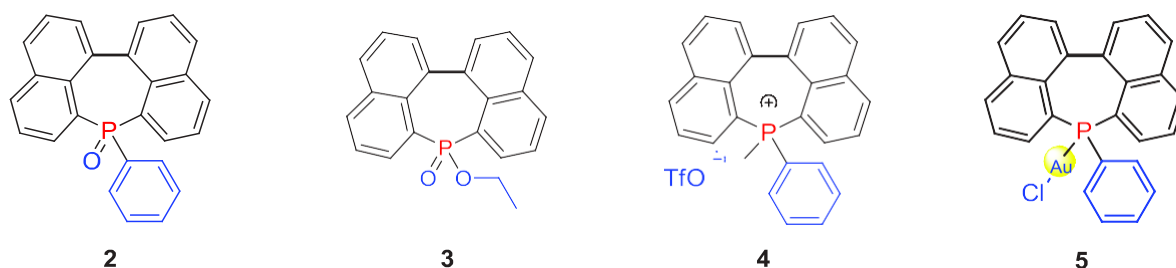


Figure 2. PAHs synthesized including phosphepines

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HYDROGENOLYSIS OF EPOXIDES BY PALLADIUM NANOPARTICLES SYNTHESISED IN WATER

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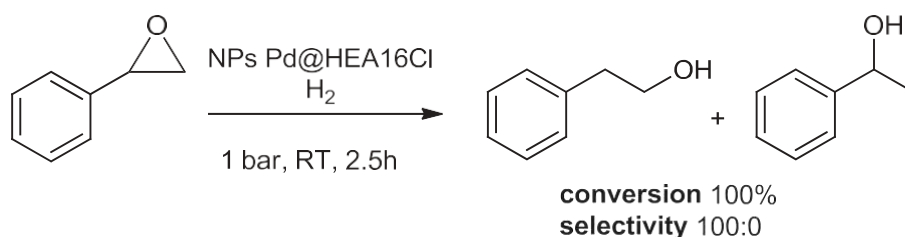
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Keywords : catalysis, nanoparticles, palladium, hydrogenolysis, epoxide, water

Catalytic methods for the selective hydrogenolysis of epoxides are highly demanded, since this reaction yields to alcohols as relevant intermediates for perfumery, cosmetics and flavouring industries.^{1,2} Historically, hydrogenolysis of epoxides was conducted with metal hydrides, which generated large amounts of toxic and polluting waste.³ In the drive towards an eco-responsible chemistry, the search of highly active and selective transition metal nanocatalysts for this process remains of great interest, as they combine the advantages of molecular complexes in regards to conversion and selectivity and the ones of heterogeneous systems in terms of convenient recycling.⁴

Well-defined transition metal nanoparticles have been easily prepared by chemical reduction of the corresponding salt, in the presence of (hydroxyethyl)ammonium derivatives as protective agent in water. They have been investigated as original catalysts for the selective hydrogenolysis of styrene oxide as model substrate. The influence of various parameters has been studied, such as the surfactant and reducing agent amounts, the chain length and the counter ion of the surfactant or the pH of the reaction medium.

Palladium nanoparticles (average diameter of 2.3 nm), stabilised by N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl)ammonium chloride salt, have exhibited excellent performances for the selective transformation of styrene oxide into 2-phenylethanol. Indeed, after 2.5 h under mild conditions and pH of 2, styrene oxide was entirely converted into primary alcohol (isolated yield of 83 %), without formation of any by-products (scheme 1).



Scheme 1: Hydrogenolysis of styrene oxide catalyzed by Pd@HEA16Cl nanoparticles

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Polyoxothiometalate-Derivatized Silicon Photocathodes for Long Lifetime Sunlight-Driven HER

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Dihydrogen production from water splitting triggered by solar-light irradiation is considered to be an attractive way to solve the increasing global energy crises in modern life. ^[1] In the thematic area of solar fuels, silicon, has appeared as the most promising material to be used as a photocathode material for the hydrogen evolution reaction (HER) because of its abundance, nontoxicity, and its tunable electronic properties. ^[2] However, this material fails to promote efficiently multielectron processes owing to slow charge transfer kinetics at bare Si and high recombination rate of electron–hole pairs generated under illumination. Consequently, the deposition of catalysts on silicon has been demonstrated as an efficient way for HER, which could help to overcome the intrinsic problems of this semiconductor serving as a photocathode. ^[3]

In this context, we have prepared p-type silicon photocathodes coated with molybdenum sulfide-based complexes, such as polyoxothiometalate electrocatalysts ($\{\text{Mo}_3\text{S}_4\}$ -based assembly incorporating the trivacant $[\text{AsW}_9\text{O}_{33}]^{9-}$ anion), which were demonstrated to be efficient for the simulated sunlight-driven HER under acid pH conditions. A superior catalytic activity and a better robustness for such photocathodes were found compared to those of the photocathodes modified with $\{\text{Mo}_3\text{S}_4\}$ clusters bearing an organic ligand. ^[4] Upon further research, the polyoxothiometalate-modified photocathode produced H_2 with a quantitative electrical yield and showed a remarkable stability during controlled-potential electrolysis tests over more than 40 h, with no visible degradation of the measured photocurrents. ^[5]

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Integrated Sensors and NanoPhotonics for Soft-matter Processes

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Abstract

During the past decade, the need of more and more precise measurements of small-scale phenomena became a major challenge for both fundamental research and industrial applications. Indeed, several fields of research such as soft matter physics, biophysics and biomedicine need to track different kinds of phenomena at the micron scale. Regarding the industrial needs, it is in certain cases crucial to monitor atmosphere composition or to detect undesirable chemical species in a solution for safety. During the past few years, integrated micro-resonators have emerged as good candidates to meet these needs thanks to the low limit of detection and the high sensitivity achievable with such devices. In this work, we present the results of the use of photonic micro-resonators for several sensing applications. The guiding structures are made of polymer DUV210 [1] and fabricated by the mean of deep-UV photolithography in a class 100 cleanroom [2]. The device is composed of an access waveguide coupled to several racetrack shaped resonators by light tunnel effect [3]. The chip is then placed on an injection bench to perform the measurements. The injection bench is composed of a broadband laser source of central wavelength $\lambda_0 = 790$ nm and full width at half maximum FWHM = 40 nm, a polarizer to TE-polarize the light and microscope objectives to focalize and de-focalize the light at the input and the output of the chip respectively. After the chip, a separating cube drives the light to both a CCD camera to monitor the injection, and an optical spectrum analyzer to measure the transduced spectra. The use of a broadband laser allow generating a frequency comb through the resonators, which is determined by both opto-geometrical features of the device and its surrounding. By depositing a reactional medium on the chip, the variations of the shape of the frequency comb is then directly related to the kinetic of the reaction. The relevant characteristics of the frequency comb to track are the free spectral range, the Q factor and the Finesse. These characteristics are directly related to physical phenomena occurring in the surrounding of the resonator so by tracking those, the following of different kinds of reaction is achievable. In this work, we present the use of integrated micro-resonators in three different applications yielding different physical properties. The first application concern the detection of sparsely concentrated glucose solution [4], the second one deals with the dynamic following of steam condensation/evaporation process and the last application is about the detection of a gel/fluid phase transition of sphingolipids [5].

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TIPS-DIAZOACETONE: NEW BUILDING-BLOCK FOR THE CONVERGENT ELABORATION OF FUNCTIONALIZED CARBON CHAINS

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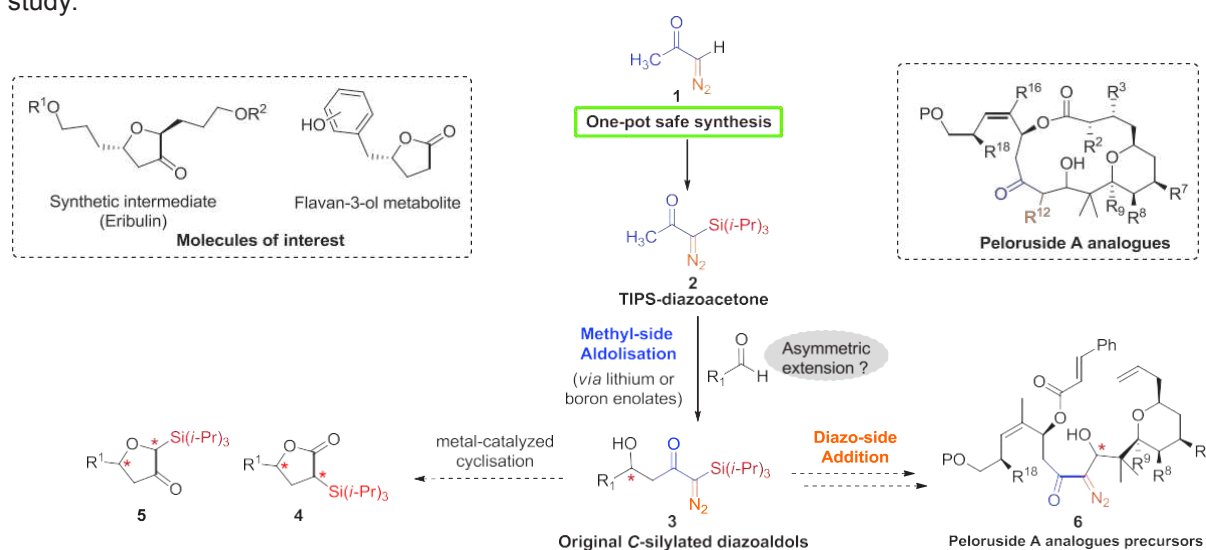
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In the frame of the multi-step synthesis of peloruside A analogues, a strong marine antitumor agent, our team is studying the synthetic potential of α -trialkylsilyl- α -diazoacetones.^{[1],[2]} These three-carbon building-blocks are C-protected on the most reactive “diazo-side” carbon by a trialkylsilyl group. The aim of this project is to study the potential of α -triisopropylsilyl- α -diazoacetone (TIPS-diazoacetone, **2**) as a pivotal three-carbon fragment, which could be inserted in a convergent way into highly functionalized carbon-chains, by “methyl-side” aldolisation and/or “diazo-side” addition,^[3] without affecting the diazo functionality. The latter is expected to constitute afterward a source of high diversity, particularly *via* intramolecular transition metal-catalyzed transformations. Original C-TIPS oxygenated 5-membered rings **4** and **5** are thus targeted, either precursors of diversely substituted butanolides, a prominent scaffold in nature,^[4] or precursors of tetrahydrofuran-3-one intermediates.^[5] Besides, the original diazoaldols **6** envisioned constitute interesting intermediates for the elaboration of new peloruside A analogues.^[6]

The first part of this work was devoted to the development of a safe method to access diazoacetone **1**, the direct precursor of TIPS-diazoacetone **2**. A convenient one-pot, three-step procedure was set up, with *in-situ* formation of the potentially explosive organic azide intermediate. The synthesis of diazoacetone **1** through continuous flow process was also studied.^[7]

The “methyl-side” aldolisation of TIPS-diazoacetone **2** was then investigated. High yields of the expected original C-silylated aldols **3** were obtained *via* the formation of lithium or boron enolates. The scope and limitations of this reaction, as well as its asymmetric extension using chiral boron enolates, is under study.



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ANALYSIS AND PREDICTION OF RESIDUAL STRESSES AND DISTORTIONS DURING WIRE ARC ADDITIVE MANUFACTURING (WAAM)

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Since the 19th century, additive manufacturing, 3D forming process by adding material layer upon layer [1], has been widely studied. Currently, powder feed additive manufacturing technologies have reached a certain maturity, that's why developing wire arc additive manufacturing (fig.1) processes appears to be necessary. Indeed, WAAM provides the advantage of generating large size components at a lower cost than with powder feed systems. However, to this day, WAAM does not lead to parts as thin, accurate and flawless than powder techniques.

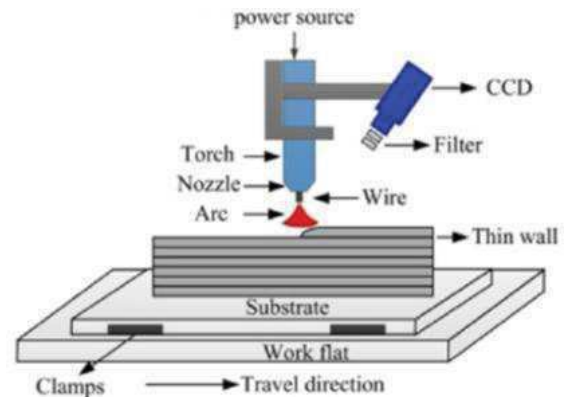


Figure 1: Principle of WAAM [2]

The WAAM technological barriers are closely bound to the operating parameters and to the thermal cycles endured by the piece during its conception. Actually, to name just one example, localized heat flow emitted by the heat source creates temperature gradients which, on one hand, have an impact on the expansion and the dilatation of the metallic material and then on the distortions and the residual stresses and on the other hand, result in phases transformations which can modified temperature distributions and generate expansion discontinuities.

This paper work deals with Gas Metal Arc Welding (GMAW) process fitted with the Cold Metal Transfer (CMT®) technology developed by FRONIUS® on the austenitic stainless steel 304L. It aims :

- In the first instance, to develop an equivalent thermal model in order to predict temperature gradients underwent metallic pieces during the operation of additive manufacturing and then to validate it thanks to the use of thermocouples and an infra-red thermal camera.
- In a second phase, to explore, by means of a design of experiments, the impact of operating parameters such as heat input, thickness of the substrate or deposition strategy on the distortions of the assembly. The deformations will be experimentally evaluated through a scanning laser.

The final purpose of this study is to conduct to the development of a multi-physics numerical model coupling thermal, mechanical and metallurgical aspects of the WAAM process which should give the possibility to foresee defects, distortions and residual stresses and thus to conceive sustainable pieces.

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DUAL-POLARIZATION FIBER LASERS FOR RADIO-OVER-FIBER ?

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In the past decades, wireless technologies have been developed to replace the wires installed in the personal network. The current Wi-Fi exploits the 2.4 or the 5 GHz bands, but because of the increasing demand, they tend to become saturated. One of the solutions is to use the millimetre-wave band, from 57 to 66 GHz, which allows a higher flow rate. However, there is high propagation attenuation at 60 GHz and non-propagation across the walls. The radio-over-fiber (RoF) connection can be used for example as a relay from one room to another, allowing broadband RF optical distribution in all the building [1]. This method requires a local oscillator (LO) which could be provided by a dual-frequency laser whose beat frequency is in the radio range.

Because of their compactness and ease of integration, we are interested in distributed-feedback (DFB) fiber lasers that can sustain the oscillation of two orthogonal polarizations at different frequencies [2]. Our work focuses on the stabilization of the beat frequency. For these structures, the beat note is in the GHz range, and first tests of the use of such a laser with RF antennas have been performed in collaboration with IETR [3]. Until now, we have tried two ways to stabilize it against a reference: one method is to use an optical phase-locked loop (PLL), by using the pump power as the birefringence actuator through thermal effects in the fiber structure [4]; the second solution is an optical frequency-shifted feedback (FSF) in an all-fibered system [5].

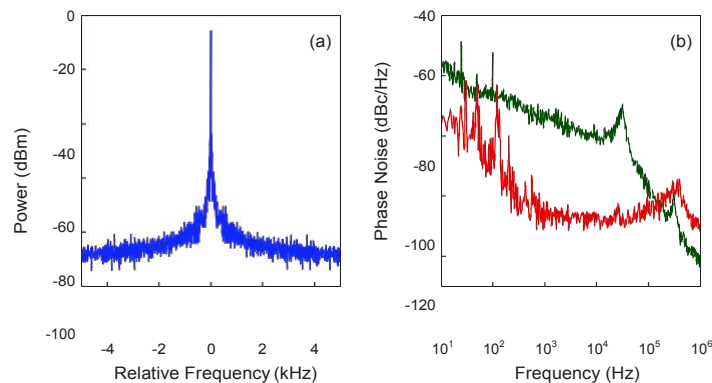


Fig.1: Stabilized beat note at 1.02 GHz. (a) Locked by FSF. (b) Phase noise spectra (green : PLL; red : FSF).

In a first set of experiments to demonstrate the stabilization methods, the free-running beat note is around 1 GHz, its linewidth is about 3 kHz and it drifts over a few MHz in hours. When the dual-frequency fiber lasers beat is stabilized (by PLL or FSF method), we find a high-spectral purity spectrum. As can be seen in Fig. 1a, the beat linewidth is measured to be as low as 1 Hz. We have compared the PLL and FSF performances. The phase noise is much lower with FSF than PLL, but the beat frequency can stay locked days in laboratory environment with PLL. For both methods, we observed a 1 MHz lock-in-range.

These results show that compact fiber lasers are attractive sources for optical delivery of stable RF signals. Of course the beat frequency must reach higher frequencies. To this aim, we plan to focus on different fiber lasers architecture (DBR, PM fiber) in the near future.

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Alkaline earth catalysts with tunable Lewis acidity for C_{sp3}-O bond activation

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The coordination chemistry of the large alkaline earths (Ae = Calcium, Strontium, Barium) remains unexplored and bears the potential for many discoveries and challenges. Ca, Sr and Ba offer advantages such as biocompatibility, high abundance, but they also present many challenges due to their reactivity, kinetic lability, polarizability, and electrophilicity. These characteristics can be adequately met by using bulky ligands that will increase the electron density at metal and stabilize them kinetically, hence yielding stable complexes exhibiting a variety of properties and applications.

In the past 10 years, we have investigated the utilization of Ae metals, and we have implemented Ae molecular catalysts for hydroamination, hydrophosphination, and dehydrocoupling reactions.¹

In the present project, Ae metals are used to generate homoleptic complexes of the form of $[(LX_2)_2Ae]$. The multidentate dianionic $\{LX_2\}^{2-}$ ligands are built on macrocycles with N, O and S heteroatoms. These ligands should be bulky enough to stabilise the complexes against dissociation via so-called Schlenk equilibria. By changing the identity of Ae metal and the number of heteroatoms in the capping macrocycle, we will generate a set of catalysts featuring tunable Lewis acidity, as exemplified in Figure 1. We have synthesized and characterized several such complexes (Figure 2). They will be used as catalysts for reactions involving C_{sp3}-O bond functionalization, e.g. coupling of alcohols with boronic acids, synthesis of cyclopentanone and pyrroles. Their Lewis acidity is being probed by 3 independent methods: the Gutmann-Becket protocol that using Et₃PO as a molecule probe,² the Childs' method,³ which uses instead cyclohex-2-enone, and a computational tool, the global electrophilicity index.⁴

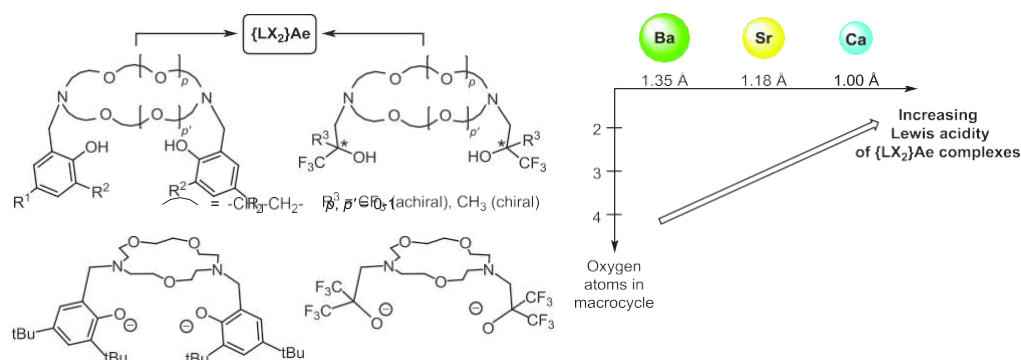


Figure 1: Synthesis of charge-neutral $[(LX_2)_2Ae]$ complexes (Ae = Ca–Ba) featuring tunable Lewis acidity

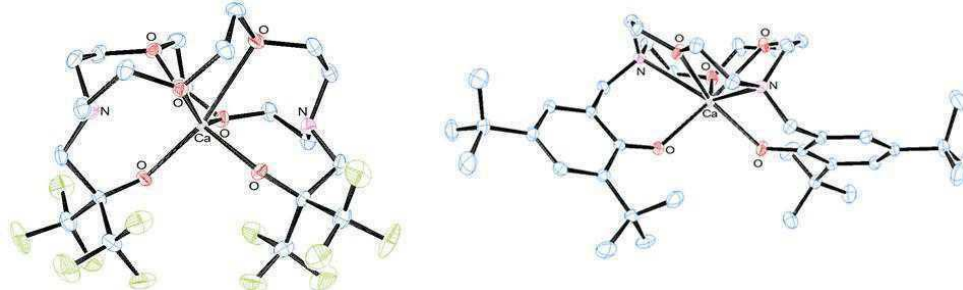


Figure 2: Examples of calcium complexes obtained so far, showing the envisaged variety of ligands and coordination sphere

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Can Toluene/n-alcohol mixtures segregate at the nanoscale?: A computational answer.

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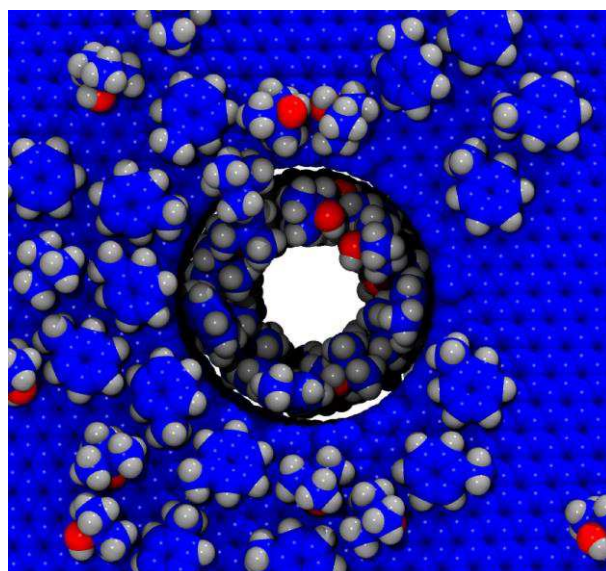
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ABSTRACT

Self-association and formation of supermolecular assemblies are important phenomena in diverse processes, from the creation of micro-emulsions to the drug delivery, to the assembly of proteins into the functional complexes, and to engineering processes. Among the self-organizing liquids alcohols are considered as models given their ability to form complex structure from hydrogen bonds. While these organizations were deeply studied these past decades in bulk phase their counter-part in nanoconfined medium was slightly investigated. Recently, it was theoretically shown that a homogenous binary mixture of *tert*-butanol (TBA) and toluene (TOL) in phase bulk can induce a strong spatial heterogeneity in confined situation¹ and probably a full demixing at the nanoscale.² Up to now the physical mechanism ruling this phase separation at the nanometric scale stays unknown. In this work, we use molecular dynamics (MD) and monte Carlo (MC) simulations to extract molecular mechanism controlling this segregation. For that extensive MD simulations of alcohol-TOL mixtures were performed in the bulk and confined phases. We focus on the structural characterization of the hydrogen bond network and its dynamics. Whereas bulk phases were strongly characterized we highlighted the possibility to control the nanosegregation at the nanoscale.

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Figure 1: Illustration of a configuration of a confined TBA/TOL mixture binary in a CNT membrane



Phase Transition and Charge Density Waves in Filled Collapsed Carbon Nanotube: An *ab-initio* study

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The spontaneous collapse of large-diameter single nanotubes (SWNTs) generates a new class of low dimensional structures, known as closed-edged bilayer graphene nanoribbons (CEBGNRs) [1]. Such innovative systems represent a rising star on the horizon of nanomaterials science, because of peculiar mechanical and electronic properties, thus holding promise as the overcoming of graphene based on high-performance nanoscale devices. Several experimental works showed that the final configurations of CLBGNs is composed by two flat nanoribbons, whose edges are closed forming chemical bonds like the standard carbon nanotubes. Our first-principle investigation based on the Density Functional Theory (DFT) revealed how these systems are mainly affected by the following parameters: initial interlayer distance, stacking sequences, and edge shapes [2]. In addition, the diameter of the carbon nanotubes plays a key role to establish the precise threshold value at which it is possible to observe the so-called structural phase transition from the classical circular shape to the new collapsed form [3]. The transition to the collapsed structure changes dramatically their electronic properties. An important advancement due to the unique architecture of these novel nanotubes is the possibility to fill the edge cavities with different molecules, observing how collapsing phase is driven by changes in the charge transfer between the chain and the nanotube and additional screening provided by the nanotube in excellent agreement with experimental measurements using the transmission electron microscopy (TEM), high resolution TEM (HRTEM), and scanning TEM (STEM) [4]. Finally, same analysis can be extended for tubes made with other materials, to example boron nitride [5].

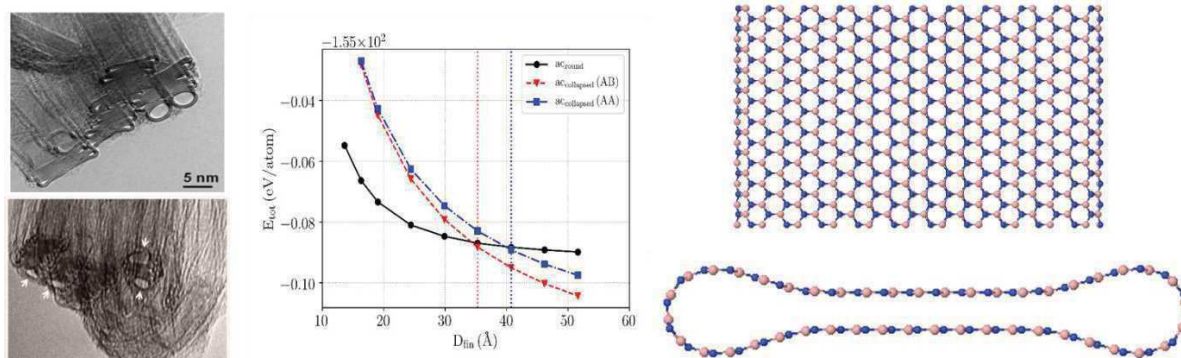


Fig. 1: TEM image of collapsed carbon nanotubes (Left). Trend of the total energy per atom of circular (black line), AB-collapsed (red line), AA-collapsed (blue line) calculated at different diameters, respectively (Centre). Different view of a collapsed nanotube made by boron-nitride (Right).

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Synthesis and characterization of plasma polymer for elaboration of vulcanization bonding.

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In many different sectors of industry as automotive and aeronautic domain, final products originate from the assembling of various materials including elastomers, like rubber. In such cases, adhesions agents are coated onto the substrate in order to establish the adhesive bonding for the vulcanization of the rubber [1]. The need for high performance has resulted in more complex deposition processes of one or more adhesive layers often run by repetitive manual coatings due to complex geometries. Consequently, the number of rejects due to poor mechanical strength induced by an inhomogeneous adhesive bond is increased. Furthermore, the primary or secondary adhesive layers are aqueous or organic liquid phases [2] containing highly toxic products. This study aims to prepare a unique bonding and homogenous layer by plasma technology which is a more eco-friendly assembly process, as a substitution of the current solution chemistry and coating procedures. In this present work, we propose to study both aspects of modification and plasma deposition on different types of substrates chosen for their wide diffusion in industrial applications or for the technological lock that it represents as PTFE. The elastomers to be vulcanized are "standard" as silicone or fluorocarbon elastomers. Treated surfaces and the obtained interfaces are characterized before the assembly. The chemical structure of plasma polymer was characterized by usual techniques such as X-ray photoelectron spectroscopy (XPS) [3] and Fourier-transform infrared spectroscopy (FTIR). The surface morphology was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM)).

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Acknowledgments



ANTICANCER DRUGS CARRIERS: NANOPARTICLES FROM DIMETHYLMALIC ACID BASED BIOCOMPATIBLE AND BIODEGRADABLE BLOCK COPOLYMERS AND HOMOPOLYMERS

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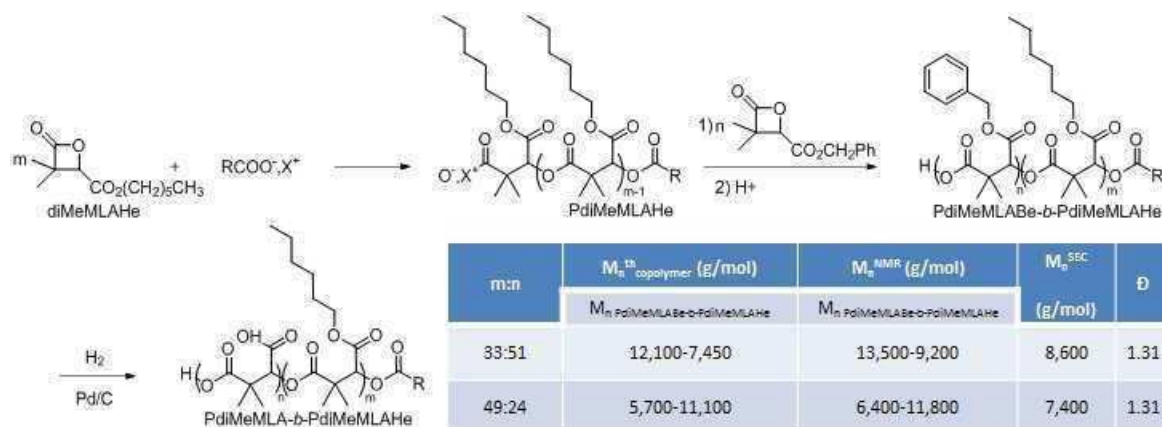
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Conventional chemotherapeutic agents have long been associated with serious drawbacks, including adverse effects on healthy tissue and the development of multidrug resistance in cancer cells. To eradicate such restraints, polymeric nanoparticles emerge as serious candidates to more specifically target tumors. In this context, amphiphilic block copolymers based on dimethylmalic acid, a biocompatible and biodegradable molecule, are very interesting candidates to prepare biocompatible nanoparticles for site-specific sustained drug delivery in the frame of cancer treatment. Therefore, we synthesized and characterized poly(benzyl dimethylmalate)-*block*-poly(hexyl dimethylmalate) by sequential ring-opening polymerization of both hexyl dimethylmalolactonate and benzyl dimethylmalolactonate. Poly(dimethylmalic acid)-*block*-poly(hexyl dimethylmalate) amphiphilic diblock copolymers were then obtained by catalytic hydrogenolysis using Palladium/Carbon as catalyst (Scheme 1).

Scheme 1. Synthesis of dimethylmalic acid-based amphiphilic diblock copolymers and their associated molecular characterizations.



Core-shell nanoparticles were prepared from amphiphilic PdiMeMLA-*b*-PdiMeMLAHe copolymers, with two hydrophilic weight fractions, by nanoprecipitation in aqueous solution. Well-defined and stable nano-objects with small hydrodynamic diameters, narrow dispersity indexes and a negative surface charge, as characterized by dynamic light scattering and zeta-potential analyses, were prepared. A hydrophobic fluorescence probe (DiR) was successfully encapsulated into these two batches of nanoparticles resulting in objects of similar hydrodynamic diameters, dispersity indexes and zeta potentials than the empty nanoparticles. *In vitro* assays (cytotoxicity and cellular uptake) on various cancer and primary cells are under study to evaluate the potential of these new biocompatible nanoparticles as drug delivery systems. Alongside, polymers are being modified to attach a target agent (peptide or sugar) for site-specific delivery of the nanoparticles to hepatocellular carcinoma (HCC) cells.

DEFECTS IN PHOTOVOLTAIC GLASS-CERAMICS MATERIALS BASED ON DOPED-Sb₂Se₃

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Defects present in the absorber layer largely dictate photovoltaic (PV) device performance: properties of defects, including bulk, grain boundary, and interface defects present in inorganic semiconductor absorbers, are crucial to thin-film solar cell performance. [1-2] In particular, defects that possess deep energy levels and large capture cross sections usually act as recombination centers, leading to severe carrier recombination loss and thus low device efficiency.

Solar cells based on Sb₂Se₃ have been reported to have an efficiency of 5.6% in 2015 [3], 6% in 2017 [4] and 6.5% later [5], thanks to its one-dimensional crystal structure, giving thin intrinsic grain boundaries, and its optimal bandgap. Sb₂Se₃ is a binary compound containing non-toxic, and Earth-abundant constituents.

It is a promising alternative absorber material for PV applications, allowing to achieve low-cost, environmental friendly and high-efficiency. It has been synthesized by using a method based on vacuum sealed silica ampoule, special attention was paid to eliminate impurities [6].

The accurate characterization of the chemical defects in Sb₂Se₃ is essential to the understanding of its transport properties (n- or p-type conductivity), but also its chemical stability. The present study combines experimental measurements and theoretical calculations.

A combined theoretical and experimental understanding on the intrinsic point defects of Sb₂Se₃ is thus urgently needed.

Different crystallographic sites, defects types (Vacancy, Substitution, Interstitial) are investigated. Software [7-8] has been used to compare formation energies, evaluate effective band structure to characterize the defects involved in the p-n junction, and obtain informations about transport properties required to have a good PV material.

The present investigation clarifies the role played by the chemical defects in this PV material and the understanding of intrinsic defects in Sb₂Se₃ film, to pave the way for further efficiency improvement of this very promising photovoltaic technology.

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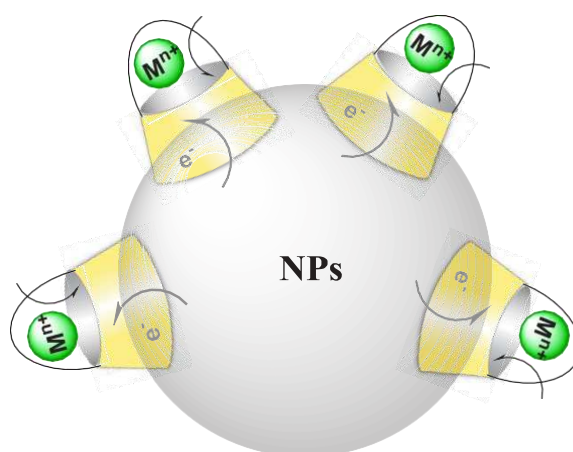
BIOMIMETIC APPROACH FOR THE ACTIVATION OF SMALL FUEL MOLECULES: TOWARDS FUEL CELL DEVICES FOR TOMORROW ENERGY

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Energy is one of the basic needs of mankind, which is crucial to sustain the daily life of people. Considering the increased industrialization of the earth's population that is forecasted to carry on growing from currently seven to ten or eleven billion inhabitants during the twenty-first century, new technologies that allow access to a clean and sustainable source of energy must be developed. Small fuel molecules such as O₂, H₂O, CO₂ or H₂ are now widely studied for reaching new low-cost and environment-friendly sources of energy. Due to their easy accessibility, use them as tanks of chemical energy, with the possibility to convert it into electrical one through their activation, is greatly desirable. However, the activation of small fuel molecules is based on multi-electronic processes that are still challenging to fully understand and apply. Nonetheless, efficient catalysis of the processes allowing activation has already been observed in nature through the action of metalloenzymes. By biomimicry, the work done in the laboratory is to develop functional surfaces with controlled interfacial properties on both nano-objects and massive materials in order to obtain an increased reactivity/selectivity with respect to these processes. Organised functionalization of the surface is obtained through the electrografting of cavitory molecules (calix[4]arene-tetradiazonium) on a catalyst surface in order to mimic the activity of metalloenzymes. The grafting will result in a highly stable monolayer, resistant to heat and chemical degradation, which can be later postfunctionalized with transition metal complexes in order to promote the activation of the small fuel molecules. Such nano-objects and massive materials should, if properly functionalized, play a key-role either in modern fuel cells or in the procedure to store the energy from chemical bonds.



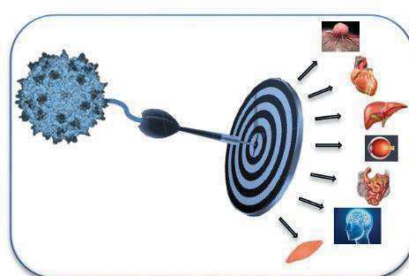
CHEMICALLY MODIFIED RECOMBINANT ADENO-ASSOCIATED VECTORS FOR SPECIFIC DELIVERY OF A GENE OF INTEREST

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Adeno-associated viral vectors (AAV) are highly efficient tools for the transfer of therapeutic genes into target cells¹. It has been shown to be effective for the treatment of genetic diseases and more than one hundred clinical trials using AAV are in progress. Those clinical trials led to the commercialization of two drugs, Glybera and Luxturna. However, despite clinical advances and the commercialization of treatments², the use of AAV remains a challenge and some limitations have been observed. For example, AAV possess a wide tropism and can be distributed to off-target cells and AAV can also be neutralized by circulation antibodies in patients, thus, preventing efficacy of the treatment. The present project aims to develop novel AAV vectors coupled to a chemical molecule to increase the target efficacy. First we selected a ligand that specifically recognize the target cell and then the ligand is coupled to the AAV capsid by a defined reactive function thanks to a click chemistry reaction. This function will allow the bioconjugation of the ligand on the virus to obtain an AAV chemically modified and achieve a better therapeutic index. During the first year of my PhD, I have synthesized several chemical compounds with the reactive function. Next, it will be necessary to couple the ligands to the AAV and demonstrate a covalent coupling. Finally, we will study of the biological properties of the chemically modified vector to transduce the target cells in primary culture and upon *in vivo* administration in animal models.

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ALKALINE-EARTH CARBODIIMIDES AS NEW POTENTIAL PHOSPHORS FOR WHITE LEDS

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Light-emitting diodes (LEDs) are emerging as indispensable solid-state light sources for the next generation of lighting. In this current era of energy saving and sustainable development, they represent a green alternative to other lighting systems used nowadays. In particular, LEDs have some advantages over fluorescent and incandescent lamps such as a better lifetime, operating voltages of a few volts, they do not emit strong UV radiations, they are mercury-free and they are almost fully recyclable. Nowadays, conventional white LEDs are made up of a blue GaN/InGaN LED chip (460 nm) covered with a yellowish emitting phosphor, cerium(III)-doped yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, YAG:Ce). Combining these two colors yields white light. Nonetheless, the light produced by such device lacks some red emission component which results in a bad rendering of the colors of the illuminated objects. To overcome these problems, the developments of red and green phosphors that can be excited by blue or ultraviolet light-emitting diodes have been largely investigated within the past decade.

This poster will focus on alkaline-earth carbodiimides which are a promising group of compounds as hosts for luminescent materials. A new facile synthetic route involving carbon nitride (C_3N_4) has been developed for the preparation of such compounds and will be illustrated by few examples such as CaCN_2 and SrCN_2 . Structural characterizations and optical properties of Mn^{2+} or Eu^{2+} doped CaCN_2 and SrCN_2 will be investigated on the bases of high-resolution X-ray powder diffraction and photoluminescence analyses to evaluate the potential of such systems as red-phosphors.

Towards a stronger halogen bond involving At – investigation of halogen-bonded adducts of AtI and Bu₃PO

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The halogen bond, a highly directional interaction between an electrophilic region of a halogenated compound (called halogen-bond donor) and a nucleophilic region in another molecule (called halogen-bond acceptor) [1], has been recognized to play an important role in a variety of fields (crystal engineering, soft materials...). Astatine (At, Z=85) is a rare radioelement belonging to the halogen group. The first halogen bond involving astatine was reported recently as the interactions between astatine monoiodide (AtI) and several Lewis bases (B) [2]. Since only a limited number of Lewis bases has been investigated so far, it is of interest for chemists to find stronger halogen-bond acceptors for AtI.

According to the halogen-bond basicity scale (pK_{B12}) that Laurence *et al.* proposed a few years ago [3], tri-n-butylphosphine oxide (Bu₃PO) was selected as a potential candidate. It is expected to possess a large $\log K_{BAI}$ value since it possesses a relatively large pK_{B12} one [2]. The liquid/liquid competition method has been applied, with an aqueous phase (HClO₄/NaI solution) and an organic phase (cyclohexane). This method consists in monitoring the distribution coefficient (D) of At-211 between these two phases as a function of the initial concentration of Bu₃PO in the organic phase. The experimental curves were reproduced by thermodynamic models involving several equilibria (occurring in the aqueous phase, in the organic phase and ruling the distribution of chemical species between these two phases).

In contrast with the previous study [2], the model involving the formation of only a 1:1 adduct (B...AtI) is not sufficient to explain the results of AtI interacting with Bu₃PO, while all the experimental outcomes can be satisfactorily reproduced by a model that includes the formation of both 1:1 adduct (B...AtI) and 1:2 adduct (B₂...AtI). The equilibrium constant ($\log K_{BAI}$) for the formation of the 1:1 adduct is 4.46 ± 0.36 , which is in good agreement with the theoretical calculations. For now, it is the strongest halogen-bond involving At that has been reported. The nature of the 1:2 adduct, which is quite original from a chemist's point of view, will finally be revealed by means of relativistic quantum mechanical calculations.

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SLIT WAVEGUIDE COUPLING SYSTEM FOR INTEGRATED MICRORESONATORS

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The conversion between telecom and datacom spectral ranges is one of the most demanded features in integrated photonic devices. The applications for photonics integrated on-chip are broad and the challenge of device scalability is of great interest for research and industry applications. Although being present in all the aspects of our life for a long time now, electronic devices still have several troubles that await to be solved. One of them is inefficiency in the routing of data through the circuits due to resistive and capacitive losses. Photonic integrated circuits will suffer much less losses and offer the advantage of multiplexing for on-chip data routing [1].

In this work we report on a slit waveguide evanescent coupler designed to maximize the optical coupling with a III-V semiconductor microdisk resonator improving the wavelength conversion efficiency. Usual evanescent coupling schemes such as all-pass or add-drop configurations can hardly minimize the coupler detuning for both wavelength ranges while preserving signals for additional losses, also when using the slit waveguide, the fundamental mode is confined in the slit allowing changes on it through modification of the slit while not affecting significantly the propagation of the second harmonic. Here, we propose the use of a slit waveguide coupler to increase the efficiency of the coupling of both, injection and extraction processes of the second harmonic generation between telecom and datacom ranges in a gallium phosphide microdisk using the propagation of the generated supermodes that exist in a slit waveguide due to the combination of the modes characteristics of a single waveguide

In microdisk resonators, nonlinear conversion processes can be magnified by the confinement of the electromagnetic fields into whispering gallery modes (WGM) and the phase matching condition can be tailored either by the $\bar{4}$ symmetry of the III-V semiconductor or by randomness of the crystal [2,3]. To maximize the coupling, a key parameter to study is the propagation constant (β) of the modes that we want to inject and extract. The second harmonic generation selection rules require to maximize the coupling of the TE (in-plane) polarized modes at telecom wavelength ($\sim 1550\text{nm}$) and the TM modes in the datacom range ($\sim 775\text{nm}$). In other words, the effective β of the WGMs, and the β of the waveguide modes should match for one polarization only for the two wavelength ranges.

The calculation of dispersion curves for microdisk and for the slit waveguide gives the opportunity to adjust the geometry of the slit waveguide in order to find the intercepts maximizing the coupling of the supermodes with the WGMs. At large wavelengths we observe the splitting of the supermode dispersion, helping a better matching of the propagation of interest. Simulation results also show a strong dependence of the propagation constant values with the geometry of the slit waveguide. The dispersion curve of a single 240 nm-thick waveguide shows the necessity of lowering down the propagation constant for the second harmonic meanwhile a larger propagation constant is required for the fundamental frequency. Making the waveguide thinner corrects this for the second harmonic modes but at the cost of decreasing the propagation constant for fundamental frequencies. We expect that a further modification of all the slit waveguide geometrical parameters will allow us to match both the telecom TE coupling and the datacom TM one.

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DEVELOPMENT OF SCANDIUM-EXOPOLYSACCHARIDE COMPLEXES AS A THERANOSTIC TOOL IN BONE ONCOLOGY

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The anti-metastatic properties of an exopolysaccharide (EPS) derivative produced by a deep-sea hydrothermal bacterium, *Alteromonas infernus*, were favorably evaluated on bone remodeling. The native EPS, called GY785, is then chemically modified by depolymerization and oversulfatation to obtain low-molecular-weight derivatives called GY785DR and GY785DRS. Asymmetrical flow field-flow fractionation (A4F) represented a worthy technique to characterize EPS. These modified EPS have anticoagulant properties and inhibit cancer metastasis. Heparin is currently used in therapy but these derivatives could represent a therapeutic alternative as well as ligands for radionuclides. The goal of this work is to scrutinize the feasibility of such coupling. Among the theranostic tracers available, scandium is of interest.

⁴⁴Sc for diagnostics / ⁴⁷Sc for therapy, is a valuable alternative to ⁶⁸Ga or ⁶⁴Cu for PET-imaging of cancer prior to ¹⁷⁷Lu- or ⁹⁰Y-based radionuclide therapy avoiding different *in vivo* uptake which is observed in these competitors due to dissimilar coordination chemistry. Moreover, ⁴⁴Sc has an isomeric state, ^{44m}Sc, co-produced with ⁴⁴Sc that can be used as an *in vivo* ^{44m}Sc/⁴⁴Sc generator allowing to study pharmacokinetics by PET imaging up to ⁴⁷Sc comparable times for optimal dosimetry.

The stability constants between these EPS with scandium have been studied. Potentiometric titration is not the most suitable technique to visualize the complexation because the stability of this sulphated EPS is limited to the short pH range of 5-8. A different analytical technique was necessary. The complexation has been assessed from a molecular point of view through Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIFS), using Eu to mimic scandium because of its fluorescence and trivalent character. TRLIFS measurements were conducted on europium with both ligands, heparin and EPS, and their isotherms have shown that complexation definitely occurs for stoichiometric ratio metal:ligand of 1:1 and it could also occur for 1:10 ratio.

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Synthesis of high purity chalcogenide glasses for Mid-IR applications

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1. Introduction

Chalcogenide glasses are promising materials for the development of step index fibers and PCFs for infrared applications, more particularly fiber mid-IR supercontinuum sources. Without any purification treatment, however, they will exhibit strong absorption bands due to the presence of impurities [1], and some of these bands will fall in the transmission window of our systems [2]. For this reason, the glasses here described are being developed using a sealed silica tube method, similar to the one described in [3]. Further optimization of the purification method is crucial for obtaining fibers which are more suitable for the intended applications.

2. Efficacy of purification in reducing losses

O-H, Se-H, As-O and Ge-O bonds, having vibrations with absorption bands in the transmission window of our glasses, are a hindrance for the development of well optimized fibers. In order to reduce as much as possible the influence of this problem, a purification with hydrogen and oxygen getters is performed during the synthesis of the glass. This induces a strong reduction in both the intensity of the absorption bands (with total disappearance of some of them) and the attenuation background in the transmission window. The purification, after the reaction of the getters with hydrogen, oxygen and water, happens in two steps: a dynamic distillation, for the removal of all the volatile impurities and a part of the solid ones, and a static distillation to eliminate the residual solid impurities.

3. Comparison between different getters

In the attempt to further improve of the purification process, different compositions and concentrations of getters need to be considered. In fact, the choice of, for example, the hydrogen getter can greatly influence the final result, as shown in [4]. In this study a comparison of the attenuation spectra of germanium-arsenic-selenide glasses prepared using different combination of getters was performed, nominally metals to remove oxygen and chlorides to remove hydrogen. The mass of getters used is kept the same in the different glasses. A strong influence of the type of getter uses on the intensity of the absorption bands can be seen.

4. Conclusions

The efficacy of the sealed tube method in reducing the amount of impurity bonds in chalcogenide glass fibers is shown. It also has a strong effect in reducing the minimum value of the losses in the transmission window to as low as 0.2 dB/m. The influence of the choice of getters on the purity of the glasses is also evidenced.

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PECVD PROCESS AND CHEMICAL SYNTHESIS TO DESIGN TiO₂/ SiO₂ NANOCOMPOSITE THIN FILMS

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During the past few decades, the Microelectromechanical systems (MEMS) have emerged in our daily life, giving us access to a wider variety of applications. Over the years, numerous attempts were reported regarding the implementation of thin films, aiming at the enhancement of optical and electro-optical devices used in these systems [1]. Taking advantage of the optical, dielectric and photocatalytic properties of titania (TiO₂) and silica (SiO₂), numerous elaborations were developed regarding the fabrication of mixed TiO₂-SiO₂ thin films, such as sol-gel [2], plasma enhanced chemical vapor deposition (PE-CVD) [3], or chemical vapor deposition (CVD) [4]. The most significant challenge in the development of such nanocomposites is to control their morphology, their growth mechanisms, the incorporation of the nanoparticles in the composite and their distribution. In view of overcoming those challenges, the present work is devoted to the synthesis of titania/silica nanocomposite thin films through an original approach. Initially, a colloidal solution consisting of crystallized anatase TiO₂ nanoparticles with a mean size of 7 nm [5] is spin coated on thermally oxidized SiO₂ silicon wafers. Second, the experimental process follows two directions: a) the plasma treatment of the spin coated TiO₂ thin films to investigate the interactions between the plasma and the films and b) the PECVD deposition in hexamethyldisiloxane (HMDSO)/oxidizing plasma on the spin-coated films, aiming at the creation of TiO₂/SiO₂ nanocomposite thin films. These two approaches were carried out in two PECVD reactors operated in different conditions: a) an atmospheric pressure plasma one using He as a working gas at the Plasma Physics Group of University of Montreal [6] and b) a low pressure one using O₂ as a working gas at Plasmas and Thin Films Group of IMN [3] under the NMC GDRi framework. Scanning Electron Microscopy (SEM) of these treated samples shows a good control over the distribution of the TiO₂ nanoparticles dispersed in the SiO₂ matrix and the impact of the plasma treatment on them. The morphology of the thin films is investigated through Atomic Force Microscopy (AFM) and the chemical analysis of their surface by X-ray Photoelectron Spectroscopy (XPS). Preliminary results obtained by Optical Emission Spectroscopy (OES) help us correlate the morphology of the treated samples with the plasma chemistry for different conditions.

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Ab Initio study of lanthanide-based Single Molecule Magnets

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In the early 90's, the discovery of polynuclear transition-metal based systems exhibiting slow relaxation of their magnetization opened a new chapter in the field of molecular magnetism.^[1] These so called Single-Molecule Magnets (SMMs) found many potential applications such as high-density data storage, spintronic or quantum computing.^[2-4] Efforts were then focused on the combination of a large ground spin state (S) and a large magnetic anisotropy (D) to reach higher effective energy barriers (ΔE) to the reversal of the magnetization (see Figure). Following this idea, lanthanide ions, with their large orbital momentum and strong magnetic anisotropy, were quickly proposed as candidates to obtain SMM properties.^[5]

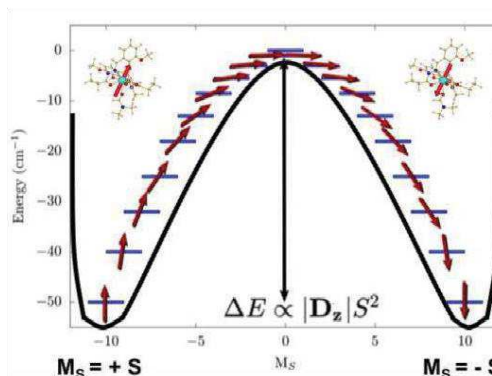


Figure: Representation of the relaxation of the magnetization through the energy barrier (ΔE) separating the two ground spin states ($M_S = \pm S$)

On the computational point of view, the multiconfigurational SA-CASSCF/(MS-CASPT2)/RASSI-SO approach is a powerful tool to obtain a good description of both the electronic and magnetic features of lanthanide-based SMMs.

The accuracy and the results obtained following this approach on several systems with various architectures exhibiting SMM properties will be discussed in this work. These structures are mainly based on the dysprosium(III) ion, one of the most studied 4f element which provide good SMM candidates.^[6] Indeed, the unique electronic structure of the dysprosium(III) ion coupled with a strong uniaxial magnetic anisotropy (Ising-type) allows the creation of a bistable ground state with a large magnetic moment ($M_J = 15/2$) exalting SMM properties in these systems.

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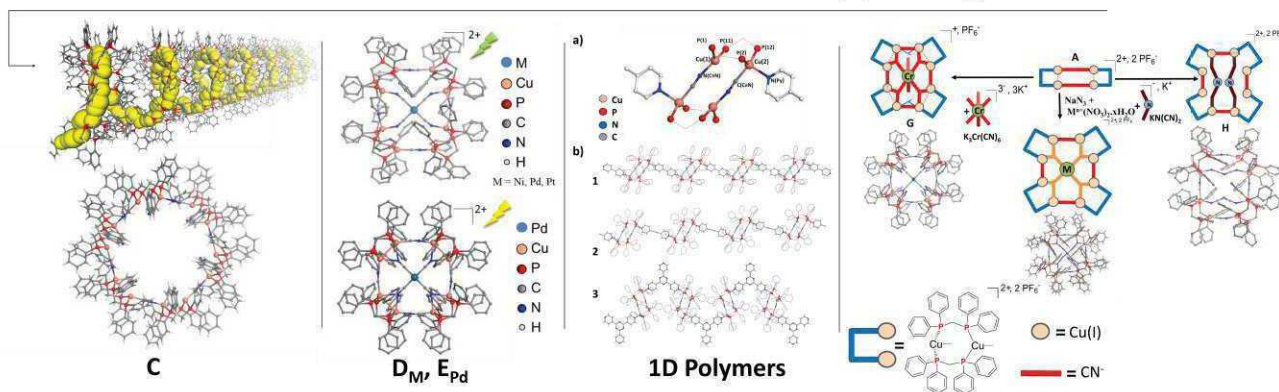
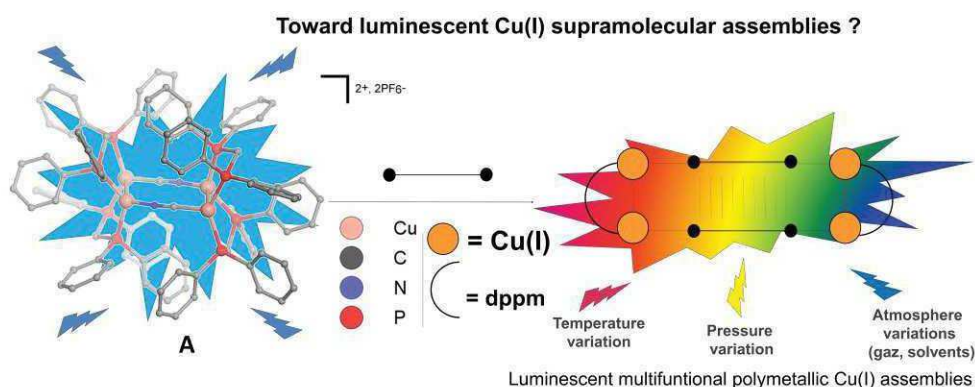
FUNCTIONAL LUMINESCENT COPPER(I) POLYMETALLIC SUPRAMOLECULAR ASSEMBLIES

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Cu(I) complexes have received increasing attention because copper is a relatively inexpensive and abundant non-noble metal and the d^{10} electronic configuration in Cu(I) ion can yield intense photoluminescence properties.¹ Recently, many Cu(I) complexes exhibiting thermally activated delayed fluorescence (TADF) have been developed and some are promising candidates for use in highly efficient, lighting and sensors applications.² In our group, we have synthesized a new series of luminescent Cu(I) polymetallic assemblies obtained using a supramolecular Cu_4 metallacycle **A**³ precursor. These compounds could present original luminescence properties (thermochromism, vapochromism and mechanochromism). Their syntheses, solid state characterization and photophysical properties will be described in this oral presentation.



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SYNTHESIS OF α -AA PEPTIDE DERIVATIVES AS PROTEIN-PROTEIN INTERACTIONS (PPI) DISRUPTORS

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Triple-negative breast cancer (TNBC) is a subtype of breast cancers and represents 15% of breast cancer cases. TNBC cells are very likely to spread and are more aggressive than other breast cancer cells subtypes with usual relapse after initial treatment. There is currently no targeted therapy available for this type of breast cancer¹. Thus, triple-negative breast cancer is more challenging to treat.

CD95L is the ligand of the death receptor CD95 which plays a role in the elimination of infected and transformed cells². This membranar ligand is mainly expressed by lymphocytes and its binding to CD95 leads to cell death through the formation of the death inducing signaling complex (DISC). By contrast, the binding of metalloprotease-cleaved CD95L (or cl-CD95L) to CD95 affords another complex called motility inducing signaling complex (MISC) involved in dissemination of TNBC cells (metastasis) as well as in chronic inflammation diseases like systemic lupus erythematosus³. So that, selective inhibition of the CD95-mediated non-apoptotic signaling pathway turns out to be a potential target against TNBC.

Among many lines of attack, we focused our attention on protein-protein interaction inhibition. Indeed, we targeted the specific interaction of CD95 with phospholipases C ψ 1, its direct effector in the MISC. Based on the peptide sequence involved in this interaction and with the help of the molecular modeling, we prepared peptidomimetics using the recent concept of α -AApeptides. These peptidomimetics have the same backbone and functional groups as conventional peptides but some amino acid side chains are transposed on the nitrogen atom of peptide bond. Thus, they should keep the biological properties of conventional peptides and should also be more resistant to proteolytic degradation⁴.

At this stage of the project, we have prepared 15 peptidomimetics and some mice experiments are underway with our 2 best compounds. We also synthesized biotin tagged mimetics to highlight the target and we currently work on building analogues to find more efficient structures.

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INVESTIGATION OF LANTHANIDE(III) COMPLEXES BASED ON PYCLEN LIGANDS WITH PICOLINATE ARMS : TOWARD LIVER CANCER DIAGNOSTIC AND THERAPY

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Hepatic cancers are hazardous to detect and to cure because of the very delicate nature of the liver in the center of the biological system. Moreover, the absence of symptoms makes the detection of hepatocellular carcinoma (HCC) late and random, which complicates the possibilities of treatment. Currently, the internal chemoembolization is the reference in terms of therapy. This method relies on the use of a cytotoxic agent that, at best, destroys the tumor, if not reduces its size to allow resection. Nevertheless, in the past few years, the internal radiotherapy procedure using α or β^- emitters demonstrated a good efficiency on the HCC treatment while being less noxious.

Lanthanide(III) ions (Ln^{3+}) are receiving great attention due to their diverse potential applications for both diagnostic and therapy. Indeed, some of them present radio-emissive isotopes ($^{90}\text{Y}^{3+}$, $^{161}\text{Tb}^{3+}$, $^{166}\text{Ho}^{3+}$, $^{177}\text{Lu}^{3+}$) useable in nuclear medicine while some others can be used for their luminescence (Eu^{3+} , Tb^{3+} ...) or magnetic properties (Gd^{3+} , Dy^{3+}). However, due to its toxicity, a metal ion can not be injected under its free form but as a thermodynamically and kinetically stable metal complex. Moreover, these complexes have to fulfill each specific application requirements.

Among various chelating agents, macrocyclic ligands such as polyazamacrocycles, judiciously functionalized, are known to strongly bind a large variety of metals. In this work, pycLEN has been functionalized with both picolinate and acetate arms, leading to neutral lanthanide complexes, which can be more retain in liver than analogous charged complexes (Figure 1) [1].

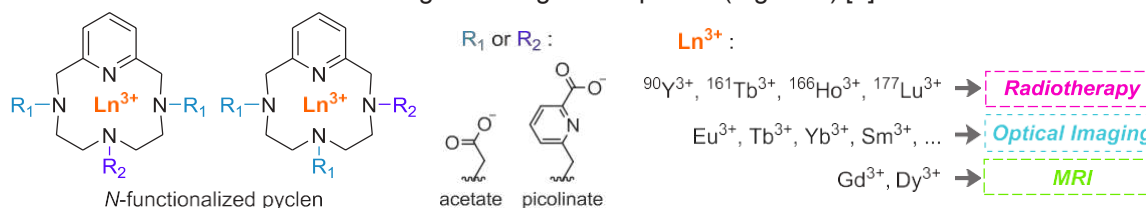


Figure 1 : Lanthanides complexes of N-functionalized pycLEN derivatives and their potential applications.

Physico-chemical and coordination properties of these lanthanide complexes have been deeply investigated, as well as the $^{90}\text{Y}^{3+}$ radiolabeling [2, 3] and the relaxivity measurements of the Gd^{3+} complexes [4, 5]. These studies confirm the great potential of these chelates for both diagnostic and therapy and lead us to take benefit of other lanthanide ions to broaden the scope of applications in the field of cancer treatment and detection.

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SILICON PHOTOELECTRODES PARTIALLY COATED WITH NICKEL

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ABSTRACT

Si is the most attractive material for manufacturing photoelectrochemical cells because it has a small band gap, it is very abundant and widely used by the microelectronics and photovoltaic industries [1]. Since Si photoelectrodes are prone to degradation in photoelectrochemical water splitting condition, it is generally admitted that they must be protected to prevent the electrical passivation or the corrosion of the surface caused by the direct exposure to the electrolyte. To achieve that goal, conformal deposition of catalytic and protective layers (e.g. Ni, TiO₂) have been widely applied on the Si surface by various vapor deposition methods [2]. Our team recently reported the excellent performance of n-Si photoanodes decorated with Ni nanoparticles (NPs) by electrodeposition [3]. Meanwhile, the origins of the performance and the stability of these electrodes were still unknown as there was no previous research on this type of electrodes. In this communication, we present an in-depth characterization study and we report the extended stability of these surfaces under illumination in operation as well as in inactivity. We show that the activity originates from the formation of a highly active catalytic Ni(OH)₂/NiOOH shell around the NPs and we finally propose mechanisms conferring the stability to the electrodes in activity and when unbiased [4].

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THEORETICAL STUDY OF THE STRUCTURAL AND REDOX PROPERTIES OF MOLYBDENE OCTAEDRIC CLUSTERS

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From R.H. Holm's work on rhenium chemistry, the implementation of clusters referred to in solid state has generated growth that can be considered at the global level of chemical clusters [1,2]. The solubility of these forms allows the formation of organic, inorganic or hybrid inorganic / organic ligands around the clusters. With the high cost of rhenium, the search for new octahedral precursors based on molybdenum was performed. Recent studies have shown that clusters of Mo_6X_{14} (X = halogen) can be dissolved and used to interact with organic and organometallic cations and / or ligands for construction by super-molecular aggregates or hybrid materials [3,4]. "Soft chemistry". Moreover, it is especially used in the development of electroluminescent diode that allows energy savings [5].

To better understand the stability of the species, the redox properties of these clusters should be investigated. Theoretical studies on isolated motifs of the general formula $\text{Mo}_6\text{X}_8\text{X}'_6$ (with X and X' halogen) are performed using DFT calculations. The variation of the electronic count of the octahedral species makes it possible to change its structural and physical properties such as symmetry, magnetic or optical properties or redox potential. Calculating these factors is a major concern for practitioners to identify the most reactive and the most stable species.

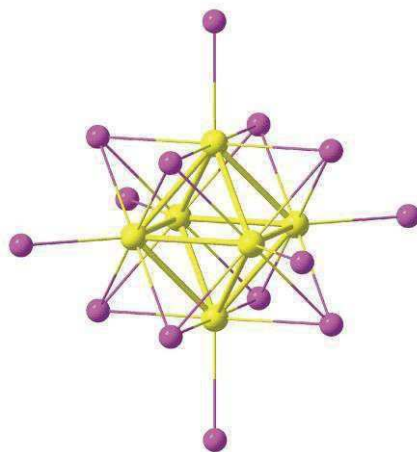


Figure 1. Faceted octahedral clusters Mo_6X_{14}

KEYWORDS: DFT calculations, electronic structure, octahedral clusters.

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LowNitrate: a passive electrochemical microbial system for nitrate removal in free surface water

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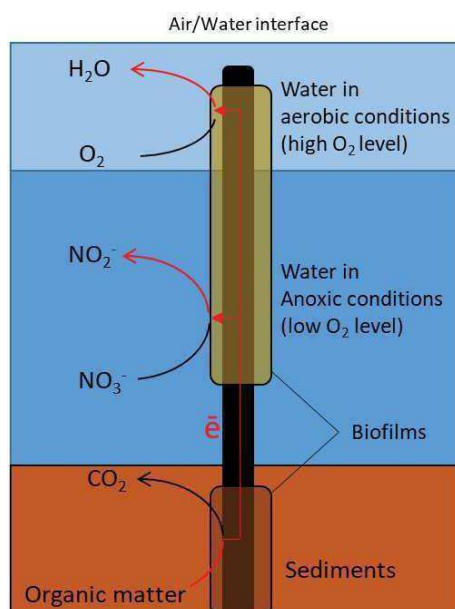
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The increase of the agricultural needs in the world led the producers to use a large spectrum of chemical compounds and fertilizers to reach higher production. This has caused pollution of rivers and aquifers, in particular with high levels of nitrate. This pollution is directly linked to the use of synthetic nitrogen fertilizers and is a major health and environmental concern.



Bio-electrochemical systems have been proposed as an innovative way to depollute different types of wastewaters but still remain to be efficiently applied outside the laboratory. Microbial Fuel Cell are bioelectrochemical systems that exploit the ability of some micro-organisms to transfer electrons obtained from oxidation of organic matter in their catabolism to a solid surface like an electrode [1]. It is also documented that some bacteria are able to accept electrons directly from a solid to reduce chemical compounds (such as molecular oxygen or nitrate) [2].

The goal of the Lownitrate project ([ANR-17-CE04-0004](#)) is to engineer a simple, passive microbial electrochemical system directly placed in the natural wetlands in order to remove nitrate. This can be achieved by inserting a snorkel electrode vertically into the sediment on the bottom (Cf. Figure) with different biofilms in the sediment and water exposed sites. This electrode has the particularity to act

both as the cathode and the anode in a short-circuit fashion. On one part of the electrode, in the sediments, a microbial biofilm oxidizes organic matter and then transfers electrons to the solid acceptor. Those electrons then flow to the other end of the electrode and are transferred and accepted by a second microbial biofilm to reduce nitrate. At the cathode electrons can also be used by other bacteria to reduce dioxygen. However, if this reduction is faster than the gas diffusion rate, it creates anoxic zones in the medium and in turn allows nitrate reduction.

To achieve this goal, experiments will be performed on site at the artificial wetland of Rampillon (Seine et Marne, France) built and managed by IRSTEA in order to mitigate agricultural pollution. The aim of the ANR Lownitrate project is to double the denitrification rate which is currently around 350 mg NO₃⁻ · m⁻² · day⁻¹.

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EFFECT OF THE SYNTHESIS CONDITIONS ON A LANTHANIDE-BASED COORDINATION POLYMER EXHIBITING BRIGHT AND TUNABLE LUMINESCENT PROPERTIES

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Over the last few years, the interest for new lanthanide-based coordination polymers (CPs) for fight against counterfeiting has significantly increased because of their luminescent properties¹. Reaction in water between the sodium salt of 4,5-dichlorophthalate (dcpa²⁻) and the heaviest lanthanide ions leads to a family of CPs with general formula Ln₂(dcpa)₃(H₂O)₅·3H₂O (Ln: Tb-Lu plus Y). This system has shown tunable and bright emission in the visible and the near-infrared regions². The presented work will show how crystallinity and morphology of the compounds are optimized by varying the synthesis conditions (concentration, temperature and reaction time).

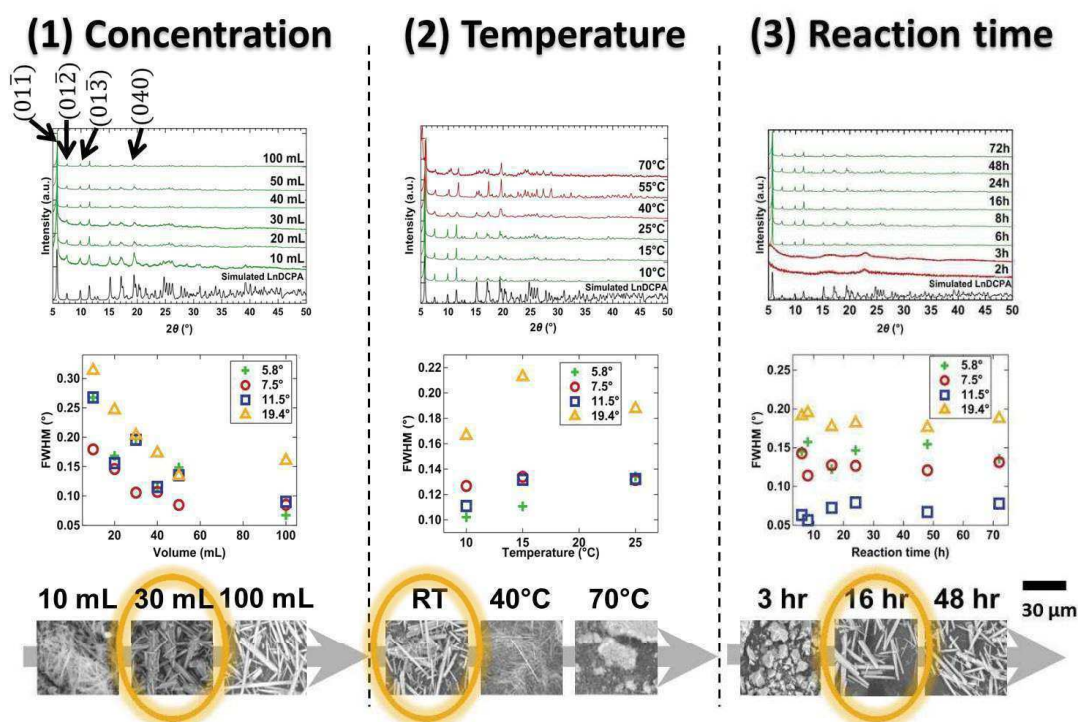


Figure: Multi-scale characterization of the Y₂(dcpa)₃(H₂O)₅·3H₂O at different concentration (1), temperature (2) and reaction time (3): Powder X-Ray Diffraction pattern (a); Full Width at Half Maximum measurements (b) and Scanning Electron Microscopy image (c)

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TREATMENT OF SIMULATED WASTEWATER ISSUED FROM A PETROLEUM ACTIVITY BY PHOTOCATALYSIS AND PLASMA

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Abstract

The petroleum industry has rooted its spot in novel trend seeking and fast-track evolving globalized world. The human greed to exploit the natural resources has increased with this trend. As a result, environmental pollution has increased, which represents a serious problem (Singh et al. 2016). Advanced oxidation processes (AOP) are generally considered for wastewater treatment (Sandeep et al. 2018). Among these processes, photocatalysis by titanium dioxide (TiO₂) has shown a considerable success in this field (Ren et al. 2015).

In this study, several operating parameters such as initial concentration of the pollutant have been investigated using a batch reactor with a fiber optic catalyst. In fact, for 16 mg/L of naphthalene and after 6 hours of illumination, the removal efficiency was around 77% and the rate of mineralization (TOC removal) was about 63%. When the initial concentration increases the availability of the active sites on photocatalytic media decreases thus leads to less degradation performance.

A pilot scale study was carried out on a recirculating reactor, several parameters (flowrate, inlet concentration) were studied. Photocatalytic degradation is almost total and reaches 96% and a mineralization of 70% for a naphthalene inlet concentration of 16 mg/L, the optimum flow rate is observed at 0.6m³/h

In order to investigate the role of radicals in the process degradation, some tests were conducted by using radical-scavengers. The addition of benzoquinone reduced the degradation rate by up to 15%. This explains the weak contribution of O₂^{•-} and HO₂[•] radicals in the photocatalytic process. On the other hand, it is noted that isopropanol has a greater effect underlining the role of the OH[•] in the degradation mechanism. For example, the degradation rate at 6 hours is reduced by about 70% when adding isopropanol.

Plasma process is also tested for the degradation of naphthalene. The experimental setup consists of a plasma generating block, the glass reactor which contains the (water /naphthalene) solution and two electrodes a high voltage electrode at the top and ground electrode at the outside bottom of the reactor. After 45 minutes of the treatment the pollutant concentration was reduced by 67% and mineralization was 64%.

In comparison with the photocatalysis the plasma seems to be more performant in term of degradation and also mineralization. However, the plasma reactor tested is smaller than photocatalysis one. More experiments will be carried out to have more accurate comparison of the two processes.

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ONLINE DEPOSITED DOSE MEASUREMENT IN PMMA USING BREMSSTRAHLUNG X-RAYS

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The detection of bremsstrahlung X-rays emitted directly by low-Z medium is a promising noninvasive technique to obtain all or part of the information of the deposited energy online [1], in hadrontherapy framework. The aim of this study is to understand the relation between the bremsstrahlung and the deposited dose in the medium. PMMA is a material largely used in radiotherapy experiment to approach a biological medium, because of its effective atomic number closed to the effective atomic number of water. The study of the bremsstrahlung signal in PMMA is interesting for future application in radiotherapy. The experimental set-up allows the irradiations of PMMA targets by alpha particles or protons delivered by the cyclotron ARRONAX (energy < 70MeV). The detection of bremsstrahlung X-rays is performed using a silicon detector. A theoretical model that takes into account the different contributions of bremsstrahlung (QFEB, SEB and AB) was used to simulate the emitted bremsstrahlung spectrum [2].

A first experiment, with 68MeV alpha particles, shows a good agreement between measured and simulated spectrums (c.f. figure). The overall number of bremsstrahlung X-rays detected for one gray received by the medium is 1060 ± 140 as compare to 970 X-rays/Gy determined by simulation. Thus, the number of X-rays per gray demonstrates a good sensibility. In order to investigate the evolution of this bremsstrahlung X-rays signal as a function of the deposited energy in the medium, experiments using different beams have been performed. The analyses are in progress and the results will be presented. These experiments are also helpful to study the predominance of bremsstrahlung components and understand the small discrepancies observed between our measured and simulated data.

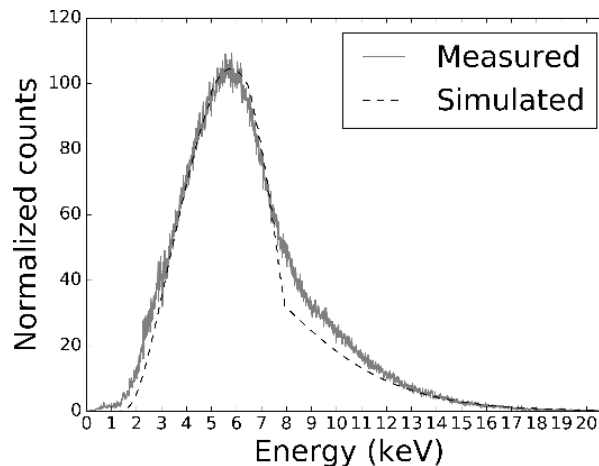


Figure: Bremsstrahlung spectrum measured (full line) and simulated (dashed line) from PMMA target.

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POLYSACCHARIDES AS INNOVATIVE RENEWABLE RAW MATERIALS FOR THE DEVELOPMENT OF GREEN/BLUE SURFACTANTS

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The development of Green/Blue surfactants based on natural renewable resources is a concept that is gaining recognition in detergents and cosmetics. This new class of biodegradable and biocompatible products is a response to the increasing consumer demand for products that are both "greener", milder and more efficient. In order to achieve these objectives, it is necessary to use renewable low- cost biomass that is available in large quantities and to design through green processes molecular structures that show improved performance, favourable ecotoxicological properties and reduced environmental impact.^[1] Within this context, marine algae and pectins represent a rich source of complex polysaccharides and oligosaccharides with innovative structures and functional properties that may find applications as starting materials for the development of green/blue surfactants and cosmetic actives. Professor Thierry Benvegnu's team at the Ecole Nationale Supérieure de Chimie de Rennes (ENSCR) is developing original surfactants based on alginates (cell-wall polyuronic acids from brown seaweeds) or pectins (structural heteropolysaccharides contained in the primary cell walls of terrestrial plants) and fatty hydrocarbon chains derived from vegetable resources. Controlled chemical depolymerizations of the algal or pectin polysaccharides give saturated functional oligosaccharides incorporating rare sugars such as uronic acids (mannuronic, guluronic, glucuronic, galacturonic acids) and neutral oses (D-galactose, L-arabinose, L-rhamnose, D-xylose). The functionalization of these oligosaccharides through transesterification/transglycosylation processes in fatty alcohols or aminolysis in fatty amines is solvent-free and yields anomerically pure ester- or amide-type derivatives.^[2] Aqueous basic and acid treatments lead to anionic or neutral single-tailed surfactants. Direct and one-pot conversion of algal or pectin polysaccharides into green/blue surfactant compositions was recently developed with a reduced cost and attractive biodegradability and ecotoxicity profiles. The industrial development of these technologies is in progress within the start-up SurfactGreen®.^[3]

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PREDICTION OF ODOR CONCENTRATION (OC) BASED ON ODOR ACTIVITIES VALUES (OAV) FOR EMISSIONS FROM COMPOSTING

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Reducing the impact of odors on vicinity from composting plants can be achieved through bio-process improvement, odor confinement and odor treatment technologies such as chemical scrubbers and biofilters. To design and support odor monitoring and mitigation plans, odors are quantified by well-established sensory methods such as dynamic olfactometry. The principal gain of this methodology is that gas samples containing the whole cocktail of released compounds are directly assessed by a calibrated human panel to measure the odor concentration (OC in $\text{OU}_E \text{ m}^{-3}$) which reflects the human detection/perception threshold to that sample; yet, odorants responsible for odor annoyances are not identified. To overcome this drawback, instrumental methods such as GC/MS and gas tubes can be used to resolve the main odorants that are present above the methods detection levels.

Compared to olfactometry, instrumental techniques are more cost-effective and not affected by human bias response. Nevertheless, chemical composition cannot stand as a sole odor indicator because compounds in the gas mixture can contribute in a different extent to the odor stimuli, depending on their odor detection thresholds (ODTs) and chemical interactions. Odor activities value (OAV) analysis is thus an alternative approach that enables to relate compounds chemical concentrations to their odorous potential. OAV is an analogous term to odor concentration defined as the ratio of compounds chemical concentration to their corresponding odor detection thresholds. Although there is a clear interest in understanding the link between OAV and sensory techniques, limited studies have explored the correlation between both approaches for environmental samples.

In this research work, the OAV feasibility to predict OC was assessed during composting of solid wastes and digestates at pilot scale. To this end, 92 gas samples from composting active phase of 9 organic matrices were analyzed by instrumental methods (i.e. GC/MS) and dynamic olfactometry. OAVs from 32 identified odorants were calculated as the ratio of compounds chemical concentrations to their corresponding odor detection thresholds (ODTs). OAVs were then correlated to OC by simple linear and partial least square (PLS) regressions. The sum of all OAVs in the gas samples (OAVsum) and the maximum OAV (OAVmax) yielded moderately strong linear correlations against OC (R^2 : 0.66 - 0.72), thus providing an overall insight into OC trend along composting. A refined PLS model consisting of weighted OAVs from 10 selected odorants slightly enhanced OC predictability. OAVs explained from 76 to 74 % of the OC variation during PLS model validation with low relative deviations in regards to 95% interval confidence boundaries (range: 0.2-26 %). By combining both approaches, OAVmax and PLS regression coefficients, four volatile sulfur compounds were found to be the principal source of odor nuisance along aerobic treatment of solid wastes and digestates: hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl sulfide. 3-methyl butanol and ethanol had a negative impact on the developed PLS model; yet, the link between this odorant and possible antagonistic effects on odor perception must be explored in future sensory experiments.

SYNTHESIS OF NANO BIOACTIVE GLASS VIA THE EMULSION PROCESS FOR USE IN BIOMEDICAL FIELD

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In 1969, L. Hench invented bioactive glasses [1] in the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5$ system. Their benefit has been widely proven in the areas of bone and dental restoration. The first bioactive glass, the 45S5 was made using the melting way. In 1991, another way of synthesis: the sol gel processing enables the fabrication of bioactive glass [2]. The synthesis by sol-gel has demonstrated advantages: a higher chemical reactivity due to the greater surface area of synthesized particles, and the possibility to obtain directly nanoscaled-particles without other manipulations (example: mechanical reduction) [3]. The possibility of using the nanotechnology approach exists in a variety of different medical applications. Indeed, nano-science is bringing outstanding value in tissue regenerative medicine. This is due to the contact between the biomaterials and the cells which are made at the nanoscale size.

In this work, sol-gel method based on the microemulsion has been used. This method makes it possible in a simple and reproducible way to produce a large quantity of nanoparticles (~ 5 g) in a relatively short period of time (1 day).

Using this process, we synthesized a bioactive glass in the $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ system. Glasses in this system have shown some potential in their properties particularly their bioactivity [4-5].

In this way, the microemulsion has allowed us to develop a new way of synthesis. The modification of parameters like such as water/oil ratio or reagents allowed us a better control of the size and an acceleration of the reaction time from 3 days to a single day.

For the characterisation of this synthesis we use Dynamic Light Scattering (DLS). It has been shown that particles can be synthesized over a range of 10 nm in the range of 20 nm to 150 nm with minor deviation (less than 10%). Furthermore the "*in vitro*" bioactivity test shows ionic exchanges with the biological environment, which is essential in this research field. Moreover, DRX results show the formation of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), which the composition is like the mineral part of human bones. Finally, cytotoxicity test has been made and allows to say these particles are not toxic for cells.

"In vivo" experiments are planned. They will take the form of powder insertion as cylindrical pellets ($d = 6\text{mm}$ & $h = 10\text{mm}$) in rabbit phrenic condyles for different duration (1 to 9 months) and will permit better understanding of the effect of glass.

Subsequently we looked for a way to improve this glass with the objective of being able to treat pathologies in addition to its ability to fill or replace bone. As a possible solution, we grafted a natural molecule for therapeutic use extracted during a collaboration at its surface to strengthen glasses healing power.

This new generation of bioactive glasses allows us to enhance metal prostheses by coating with these glass particles. This enhancement may allow a better integration of prosthesis in the body and does not engender any problems with possible rejects or infections from graft.

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FIRE RESISTANCE IMPROVEMENT OF PLASTERBOARD BY REFLECTION OF THERMAL RADIATIONS

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Fire resistance of construction materials used to be only studied considering the convection dimension of a fire. However, in addition to the heat created by the fire, flames emit infrared radiations whose wavelength depends on the temperature. This radiative part is usually neglected in the degradation process of the material. Yet it is said that a construction element from 0.5 m away from the fire is more damaged by the radiation than by the heat convection [1]. So an increased reflectivity of the material should reduce the amount of IR radiation absorbed, thus improving the fire resistance. As part of the study a measuring bench has been developed to assess reflecting performance of construction materials like plaster.

In France fire resistance tests are normalized especially by a curve known as ISO 834-1 [2]. It shows the speed of the temperature increase that has to be followed during the experiment. Based on this curve and our experience of those tests, a temperature domain has been selected where most of the degradation occurs: [700°C; 1000°C]. The blackbody calculation (Planck's law) deduced from those temperatures defines our work interval (Figure 1).

The reflectivity improvement must be efficient on this wavelength range.

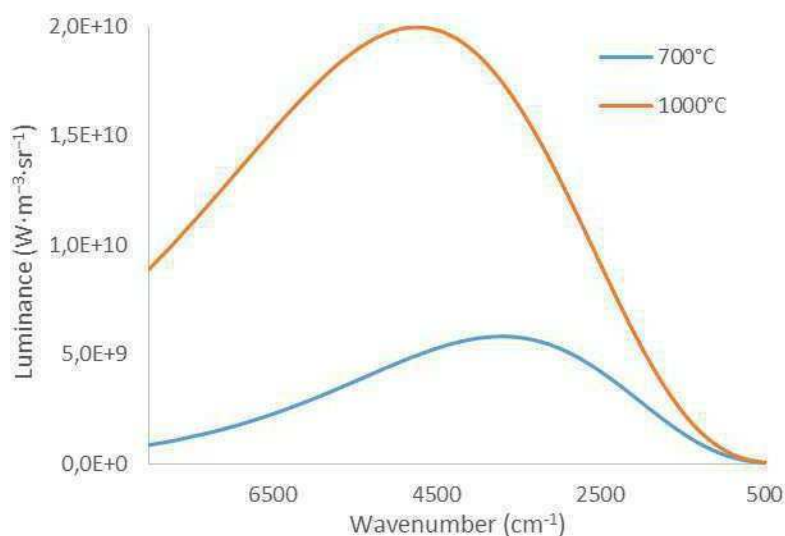


Figure 1: Blackbody radiance at 700°C and 1000°C

In the meantime a list of different solutions to be tested is made on the basis of literature. Because of the extreme conditions that are those of the fire, organic coatings have to be avoided. This poster will show the improvements in fire resistance that can be achieved by following our strategy.

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Preparation of the Calcium complexes

stabilized by C-F secondary interaction

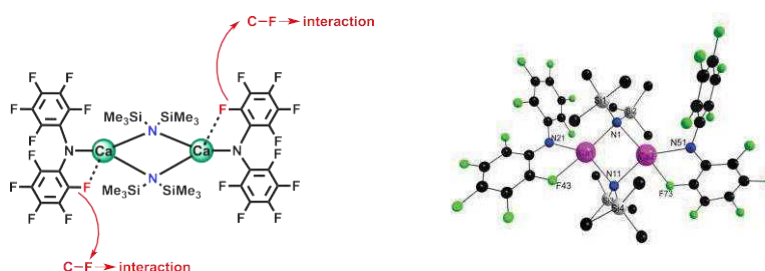
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Synthesis and isolation of alkaline earth heteroleptic complexes with the general form of LAeNu (L: supporting ligand and Nu: reactive ligand) is challenging according to their instability regarding to the characteristics such as oxophilicity, electrophilicity and polarizability. Their high ionic radii requires high coordination numbers, which is also the reason of presence of the solvents such as tetrahydrofuran, in the related crystal structure in some cases and is not ideal in catalytic process. We have proved that noncovalent secondary interaction of $Ae \rightarrow F-C$ plays an important role in creating new Ae heteroleptic species which could generate sufficient coordination number around the metal center and therefore provide enough stability for the complex without the coordinating solvent. [1] To achieve the target complexes we have used an aromatic fluorinated ligand. The obtained X-ray structures show short distances and therefore strong interactions of the metal center with the F – bond and how they contribute to stabilize the compound. [2-3]



The reactivity of the new fluorinated complex has been evaluated by application of the bulky ligands such as β -diketiminato (BDI) and iminoanilide type of ligands which could provide enough bulkiness around the metal center and increase the stability. [4-5] The fluorinated ligand plays the bridging role in these structures. We have been developing the research over the new fluorinated ligand which could be more active and efficient in catalysis alongside with the extra stability provided by the secondary interactions.

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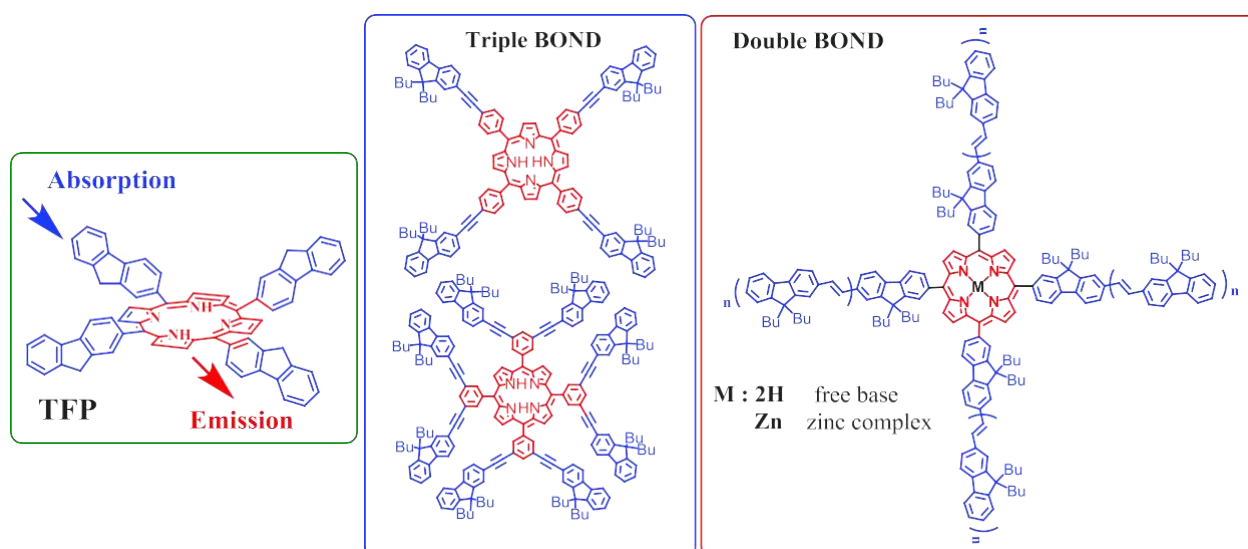
OPTICAL PROPERTIES OF NEW FLUORENYL PORPHYRINS

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Since 2004, we are interested in the optical properties of fluorenyl-porphyrins because we found that **TFP**, a porphyrin possessing four fluorenyl arms^[1], exhibits a high fluorescence quantum yield (24%) compared to the reference tetraphenylporphyrin (**TPP**), demonstrating the good capacity of the fluorenyl units to enhance fluorescence quantum yields.^[2-6] So first, we synthesized a series of porphyrin dendrimers with fluorenyl arms connected by *non-conjugated* ether linkers.^[7] In 2016, to improve these systems, a second group of porphyrin dendrimers fully *conjugated* with alkynyl linkers was obtained (**Triple Bond** as described in Figure), and their photophysical properties were ameliorated.^[5] Very recently, to improve these **Triple bonded** systems, **Double bonded** porphyrins are elaborate because of better conjugation than triple bond porphyrins.^[8] Based on **TFP**, we designed a series of new porphyrin compounds containing a larger number of fluorenyl antennae connect by various linkers, in order to make these porphyrins appealing for 2-photon based photodynamic therapy (PDT) and bio-imaging.



Fluorenyl Porphyrins: TFP, Triple bond Dendrimers and new double bonded Porphyrins

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INVESTIGATING THE INTERACTIONS AT THE INTERLEUKIN-15/IL-15RB INTERFACE THROUGH MOLECULAR DYNAMICS SIMULATIONS AND VIRTUAL SCREENING

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The Interleukin 15 (IL-15) is a cytokine involved in a plethora of different cellular functions. It participates in the development and activation of immune responses. Its functions include the stimulation of memory T cells and NK cell proliferation and activation, as well as the inhibition of the apoptosis in immune cells. IL-15 has therefore clearly appeared as a potential target for several therapeutic applications. [1]

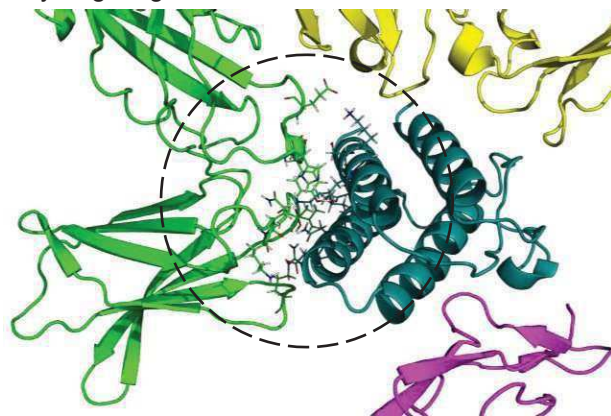
The structure of this cytokine is based on a quaternary complex between IL-15 and its α (IL-15R α), β (IL-15R β) and γ (IL-15R γ) receptors. The key to the functional modulation of IL-15 lies on its interaction with its receptors. A comprehensive understanding of the structure and behavior of the IL-15/IL-15R β interface is therefore an important issue. In the framework of a multidisciplinary consortium established with biologists and organic chemist partners aiming to design inhibitors of selected IL-15/IL-15R interfaces, we address this issue through molecular dynamics (MD) simulations.

In this work, MD simulations have been applied on different IL-15 multimeric models in order to investigate the time-related behavior of the various systems. More precisely, our objectives are (i) to characterize the corresponding structural fluctuations (ii) to determine the key components (amino-acid residues, water molecules) of the IL-15/IL-15R β interface (iii) to highlight and quantify the key interactions. This work will not only provide a complete and accurate picture of the different interfaces behavior: it will also serve as a link with the Virtual Screening campaign that follows.

Since there are not, currently, any known modulators of IL-15, the data obtained from the MD simulations, namely the key residues and relative importance of the residue pairs, will play a key role in developing and validating the Virtual Screening protocol.

Starting from the crystallographic data (Tetramer PDB ID: 4GS7) [2] and performing MD simulations with the NAMD program using the CHARMM3 force field for 100 ns, our methodology is validated through the good agreement between the specific interactions found in our models and the ones reported from experimental studies (e.g. Glu64-Arg45 in the IL-15/IL-15R β interface). Furthermore, our results allow deciphering the relative importance of the various interactions. Lastly, relevant and specific interactions have been pointed out at the interfaces, such as a water molecule mediating interactions involving several key residues. The identified region has been used to perform a Virtual Screening campaign, using LigandFit.

Our work provides a more realistic picture of the IL-15 system structural features and highlights new key components of the various interfaces. These data will be useful for the design of highly specific small organic ligands selectively targeting the different interfaces.



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SYNTHESIS OF LUMINESCENT MOLECULES BASED ON TRIAZINANE-2,4,6-TRIONE AND STUDY OF THEIR OPTICAL PROPERTIES

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Materials presenting two-photon absorption properties are currently of high interest, due to their potential applications in various fields, such as 3D-microfabrication, medical imaging and photodynamic therapy for instance.¹ 1,3,5-Triphenyltriazinanes-2,4,6-triones, more commonly known as triphenylisocyanurates, have been reported by some of us as exhibiting remarkable one-photon and two-photon absorption properties.²

In this project, we synthesized two series of triaryl isocyanurate chromophores, with benzenes or thiophenes in the conjugated arms, and with different kinds of end-groups (donors or acceptors), in order to study their performance in optics.

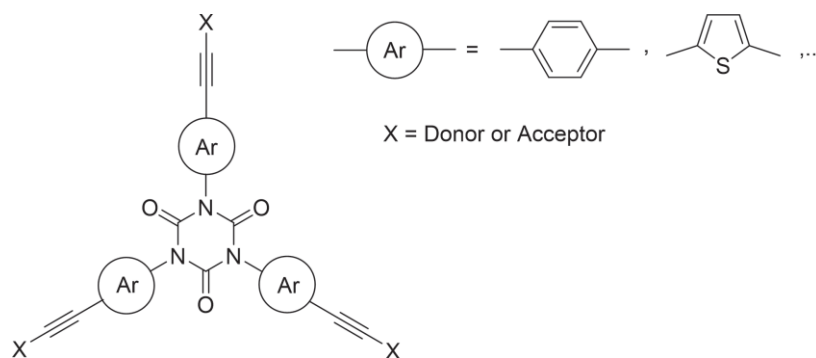


Figure 1 Molecular Structures of isocyanurate-cored chromophores

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HETEROMETALLIC GOLD-PORPHYRIN-PLATINUM CONJUGATES. SYNTHESIS, CHARACTERISATION, CYTOTOXICITY AND PHOTOTOXICITY STUDIES.

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Cisplatin is one of the most effective anti-cancer drugs and is used in almost 50% of anti-tumoral chemotherapies. However its clinical use is limited by several toxic side effects [1]. Gold complexes, and especially porphyrins metallized by gold (III), have emerged as another family of metallo-drugs with very encouraging cytotoxic properties [2], in addition, several teams of researchers have worked on the combination of several coordination complexes (Gold / Pt for example) in the same molecule, in order to improve their activity due to the synergistic action of the two drugs with multiple biological targets [3]. In the same vein, the combination of a porphyrin system and a platinum complex in the same molecule should lead, on the one hand to the combination of the photodynamic activity of porphyrin and the cytotoxic activity of platinum, and on the other hand to the enrichment of tumors by the porphyrin-platinum hybrid due to the affinity of porphyrins for cancer cells [4]. Indeed, porphyrins would be promising candidates to carry cisplatin or any other cytotoxic agent in cancer cells.

Our approach is to combine cytotoxic coordination complexes (Cis-platinum complex, titanocene, ruthenium or gold complex) with gold porphyrins within the same molecule (Figure 1). These hybrids gold porphyrin/ coordination complex, should exhibit the cytostatic activity of the coordination complex in the dark and be amplified by the photodynamic activity of the gold porphyrin under light irradiation. In a second step, we planify to extend this strategy by replacing the porphyrin with a chromophore having absorption bands located in the window of transparency of biological tissues (700-900 nm). This in order to be able to act on tumors of significant sizes due to a deeper penetration of the irradiation light.

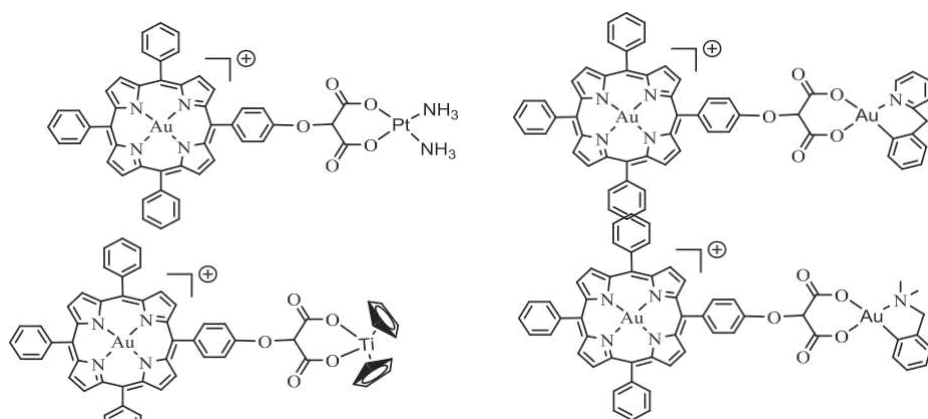


Figure 1: Structures of some hybrid molecules considered in this project.

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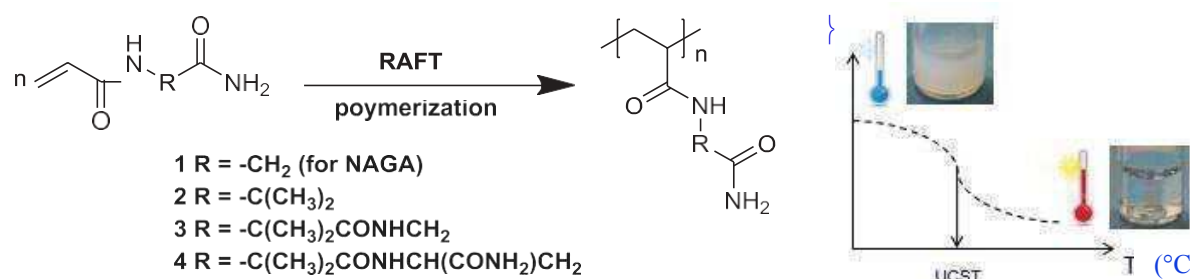
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Synthesis of UCST-type thermosensitive polymers by thermal and photo-RAFT polymerization

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Up to now, just a few polymers were known to show an upper critical solution temperature (UCST) in water. An UCST arises from strong polymer-polymer and solvent-solvent interactions compared to weak polymer-solvent interactions. It can rely on hydrogen bonding or Coulomb interactions. Most applications require a stable UCST phase separation accurately predictable under varying conditions rather than being influenced by a multitude of factors. In this context, we believe that hydrogen bonding-UCST polymers are more promising than Coulomb interactions-UCST polymers. Although poly(N-acryloyl glycinamide) (PNAGA) is known for decades, its UCST behavior had not been reported until 2010.ⁱ Phase separation of PNAGA synthesized by conventional radical polymerization, is triggered by the intra- and intermolecular formation of hydrogen bonds between the donor and acceptor sites of the primary amide groups. When PNAGA is synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT), the UCST behavior was not obvious in aqueous medium.ⁱⁱ Our study focused on synthesis of PNAGA illustrating UCST properties by thermal and photo-RAFT polymerization from different initiators and chain transfer agents (CTA) (Scheme 1). The UCST was investigated by turbidimetry, regarding the influence of the nature of initiators and CTAs. Furthermore, other acrylamide monomers with similar chemical structures as NAGA also were polymerized *via* the RAFT process to search for new UCST polymers.



Scheme 1. Synthesis of UCST-type thermosensitive polymers by RAFT polymerization

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INHIBITORS OF RAC1 PREVENT SEVERE ALLERGIC ASTHMA

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Allergic asthma is a major public health problem. It affects 230 million people in the world, and kills 180 000 asthmatics each year. An asthma attack is characterized by the inflammation and a chronic bronchial obstruction associated with airflow alteration (Fig. 1). It can be treated using corticoid or bronchodilators. However, 20 % of severe asthma cases do not respond to such medication and thus require urgent investigations.

Within this framework, the PIRAMID program offers an expertise in the field of protein-protein interactions (PPIs). Proteins are involved in many cellular processes and this appear as appealing new targets, especially in the field of respiratory diseases.

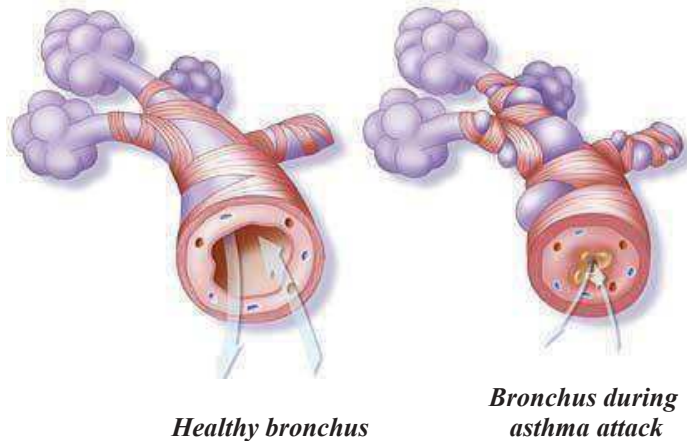
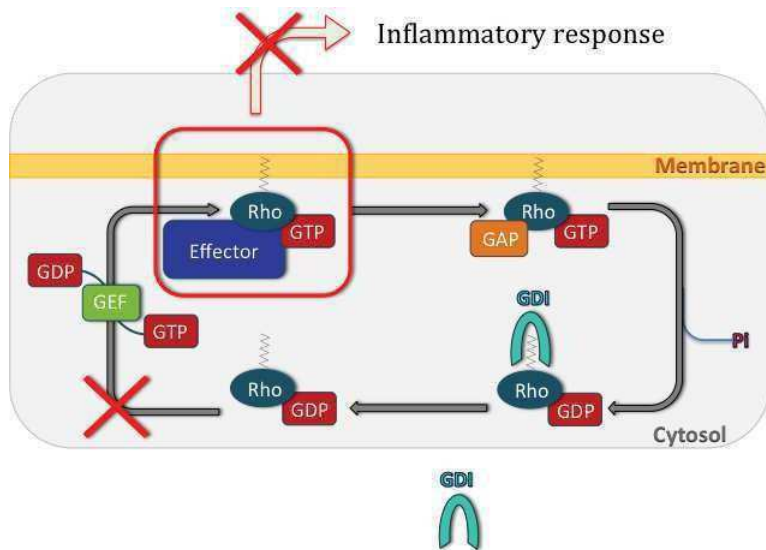


Fig. 1: Scheme of healthy bronchus vs asthmatic bronchus.

The PIRAMID program pools together 3 areas of expertise including modellers, biologists and chemists. In a hit-to-lead strategy, this trio interacts in order to find a drug able to cure asthma. It has been recently shown that Rac1 protein is involved in the bronchus contraction during an asthma crisis.^[1]



This GTPase, belonging to the Rho proteins' family, acts as a binary switch to control many fundamental cellular processes such as cytoskeleton organization, gene expression, cell cycle progression or cell motility and contraction. The Rho proteins' activity results from a tightly regulated balance between the GTP-bound (active state) and the GDP-bound (inactive state). Catalysing the exchange from GDP to GTP, Rho guanine exchange factors (GEFs) are major regulators of Rho proteins' activity. Thus targeting the interaction of Rho GTPase with its GEFs appears as an alternative strategy to block Rho protein signalling in a specific manner, improving its druggability (Fig. 2).^[2]

During this poster session, I would like to show you what my job as PhD student in the PIRAMID program consists. Explaining how it is possible to design an innovative drug, from its synthesis to its evaluation and optimisation.

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Synthesis of new immunadjuvants based on rare fluorinated carbohydrates

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Summary: Carbohydrates are interesting targets for the development of new bioactive agents. They are the most abundant organic molecules found in nature. Unlike hexopyranoses, hexofuranoses are absent from mammals but they can be found in cell wall bacteria, fungi and parasitic microorganisms.^[1–3]

Fluorine is more and more used in pharmaceuticals products because of its properties (perturbation of pKa, modulation of lipophilicity, electrostatic interactions ...), and its size, it can substitute H or OH group in molecules with minimal steric perturbation.^[4–6]

Enzymatically synthesized fluorinated galactofuranosides (Gal_f) showed attractive biological properties, in particular on macrophages and dendritic cells.^{7,8} To pursue in this direction, several mono- and difluorinated galactofuranosides were synthesized. Galactose was forced in the furanose configuration and its hydroxyl groups were protected in order to graft the fluorine group on C-6. Two different donors, a thiophenyl Gal_f and a Gal_f bromide, were tested in glycosylation reactions. Three different products were identified following the glycosylation, two disaccharides linked in (1,2) or (1,3) and one trisaccharide linked in (1,2) and (1,3).

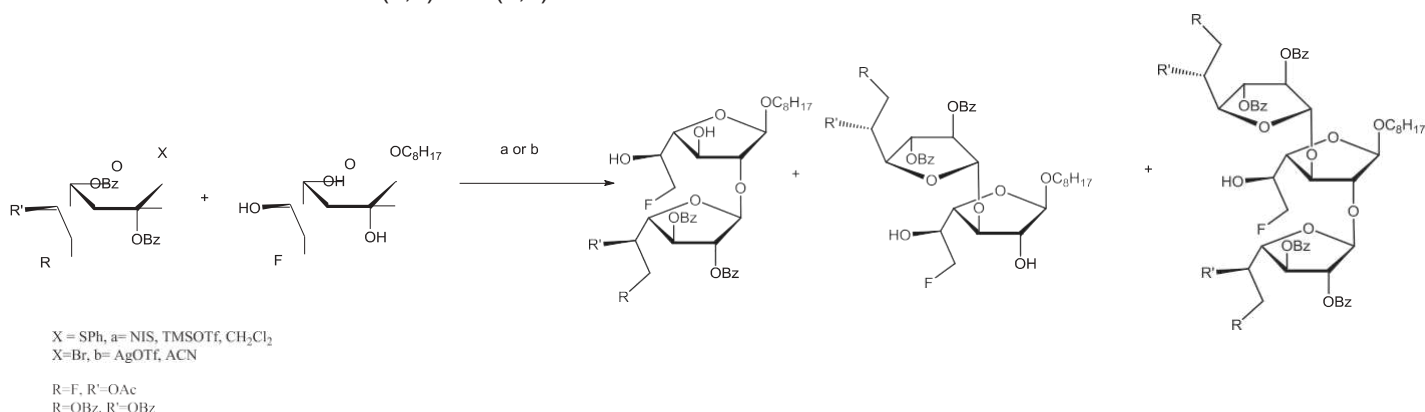


Fig. 1 Glycosylation between a fluorinated donor and a fluorinated acceptor

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IMPACT OF HETEROCYCLIC ANALOGUES OF SKF-96365 ON ORAIS FOR SOCE INFLUX INTO ION CHANNELS.

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This work deals with the synthetic development of SOCE influx inhibitors (Store Operated Calcium Entry) targeting Orai1 transmembrane proteins in cancerous cells. Orai proteins are considered as potential therapeutic targets in breast cancer but also in prostate cancer, colon, lung or glioblastoma. Three inhibitors of these channels are known to date namely SKF-96365¹ (non-selective ion channel inhibitor known since 1990), GSK-7975A and Synta 66 (non-selective ion channel inhibitors). For our work, we selected SKF-96365 inhibitor because this one is commercialized and used as a probing tool for SOCE assays since the 1990s, although it is worthing to note that this inhibitor is a racemic mixture, that means the SOCE assays is not dependant of the chirality of the inhibitor. In this context, our laboratory has developed several series of SKF-96365 analogues² and in 2015 the inhibitor DAD3.473 has been identified as "linear" SKF-96365 analogue³. With the aim of understanding better the mechanism of action and calcium cellular regulation of these inhibitors, we developed in a first approach hybrid inhibitors of DAD3.473 associated to moieties issued from GSK- 7975A and Synta 66 inhibitors⁴. Then in a second phase, we investigated a structural regression of the side chain of DAD3.473 in order to understand the mechanism of this new inhibitor towards Orai1 proteins in SOCE influx, particularly the impact of the phenol moiety⁵. To complete the mechanism study of these inhibitors, we are currently conducting a multistep synthesis work of fluorescent probes (NBD fluororescent labelling or other) attached to the inhibitor bearing various heterocyclic platforms, the underlying idea is to better understand the mechanism of action (ligand / protein interaction) of these Orai1 inhibitors by fluorescent assays in cell cancerous (lymphoid cells or adherent cells). We hope that study of fluorescent labelling, will allow us to improve the molecular design of our inhibitors and to identify a "lead" inhibitor. This "lead" would allow us to envisage assays on an animal model.

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² a) Camille D. Dago, Paul Le Maux, Thierry Roisnel, Christophe Brigaudeau, Yves-Alain Bekro, Olivier Mignen, Jean-Pierre Bazureau. *Int. J. Mol. Sci.* **2018**, 19, 856-879. doi:10.3390/ijms19030856. b) C.D. Dago, P. Le Maux, T. Roisnel, C. Brigaudeau, Y-A. Bekro, O. Mignen, J-P. Bazureau. *2nd International Caparica Christmas Congress on Translational Chemistry 2017 Proceeding Book*, p 83. ISBN: 978-989-54009-1-1

³ Camille D. Dago, Christophe Brigaudeau, Yves-Alain Bekro, Olivier Mignen, Jean-Pierre Bazureau. Unpublished work, manuscript under progress.

⁴ Camille D. Dago, Voli Lou-Anna, Christophe Brigaudeau, Yves-Alain Bekro, Olivier Mignen, Jean-Pierre Bazureau. Unpublished work, manuscript under progress.

⁵ Camille D. Dago, Christophe Brigaudeau, Yves-Alain Bekro, Olivier Mignen, Jean-Pierre Bazureau. Unpublished work, manuscript under progress.

SYNTHESIS AND CHARACTERIZATION OF COORDINATION POLYMERS: PROBING PHOTO-PHYSICAL PROPERTIES

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Lanthanide based coordination polymers have attracted great attention because of their various structures and physical/chemical stability.^[1] As far as luminescent properties are concerned, lanthanide coordination polymers present interesting and characteristic properties such as color purity, long lifetimes and high quantum yields due to their sharp $f \rightarrow f$ transitions.^[2]

In this study, we synthesized a series of isostructural compounds with general chemical formula $\text{Ln}_2(\text{mip})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$ where H_2mip stands for methoxyisophthalic acid.^[3] Luminescent properties of hetero-metallic compounds were studied. Three series of hetero-metallic compounds : $\text{Gd}_{0.2}\text{Tb}_{1.8-2x}\text{Eu}_{2x}(\text{mip})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$, $\text{Gd}_{0.2}\text{Tb}_{1.8-2x}\text{Dy}_{2x}(\text{mip})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$ and $\text{Gd}_{0.2}\text{Eu}_{1.8-2x}\text{Dy}_{2x}(\text{mip})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$ ($0 \leq x \leq 1$) will be presented.

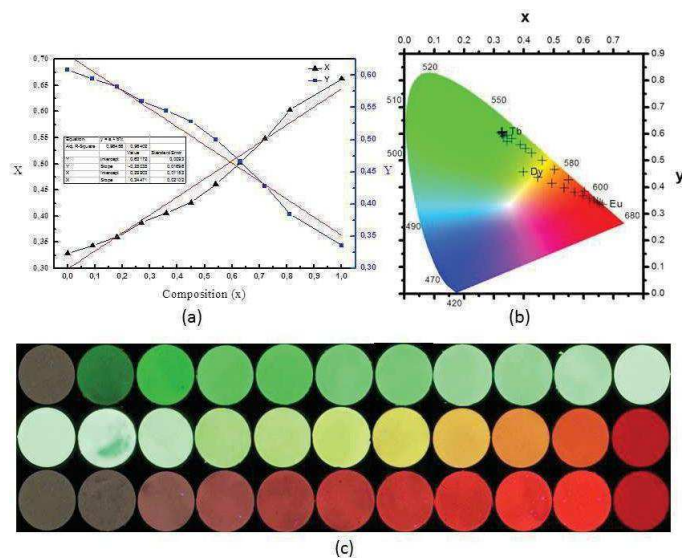


Fig 1. (a) Linear relation between the composition and the x,y colorimetric coordinates in the $\text{Gd}_{0.2}\text{Tb}_{1.8-2x}\text{Eu}_{2x}(\text{mip})_3(\text{H}_2\text{O})_8 \cdot 4\text{H}_2\text{O}$ series; (b,c) the colorimetric coordinates and pictures of the three series of compounds under UV radiation.

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Synthesis, structure and luminescent properties of new hexa-lanthanide compounds based on hexa-nuclear oxo-hydroxo rare earth entities

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The synthesis of new hexa-lanthanide compounds based on hexa-nuclear rare earth entities with general formula $[\text{Ln}_6\text{O}(\text{OH})_8(\text{NO}_3)_6(\text{H}_2\text{O})_n]^{2+}$ used as precursors have been studied by our group since more than 10 years [1-5]. Recently, we succeeded in synthesizing three unprecedented families of iso-structural hexa-lanthanide compounds by reaction of rare earth hexa-nuclear octahedral molecular precursors with 3-chlorobenzoic acid, 3-iodobenzoic acid or 3-bromobenzoic acid as ligands in acetonitrile medium via solvothermal or microwaves assisted syntheses. Their chemical formulas are $\{[\text{Ln}_6(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2(3\text{-cb/bb/ib})_{14}] \cdot (\text{CH}_3\text{CN})_n\}$ (Fig.1) where $n=4$ or 6 ; 3-cb/3-bb/3-ib stands for ligand 3-chlorobenzoate, 3-bromobenzoate and 3-iodobenzoate respectively and $\text{Ln} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Gd}^{3+}$, plus Y^{3+} . In addition we have obtained 4f-4f' compounds with a similar procedure by using the appropriate mixture of rare earth ions. Their chemical formulas are $\{[\text{Ln}_{6-6x}\text{Ln}'_{6x}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2(3\text{-cb/bb/ib})_{14}] \cdot (\text{CH}_3\text{CN})_n\}$ where $n=4$ or 6 ; $\text{Ln}=\text{Eu}/\text{Tb}$, $\text{Ln}'=\text{Tb}/\text{Y}$ with $0 \leq x \leq 1$. These compounds were studied with the aim of characterizing the energy transfer between rare earth ions together with the possibility of tuning the emitted color. Moreover, we have also studied the optical properties of these compounds in solution, and have proven that hexa-lanthanide cores were not destroyed. This result is of great significance for our research.

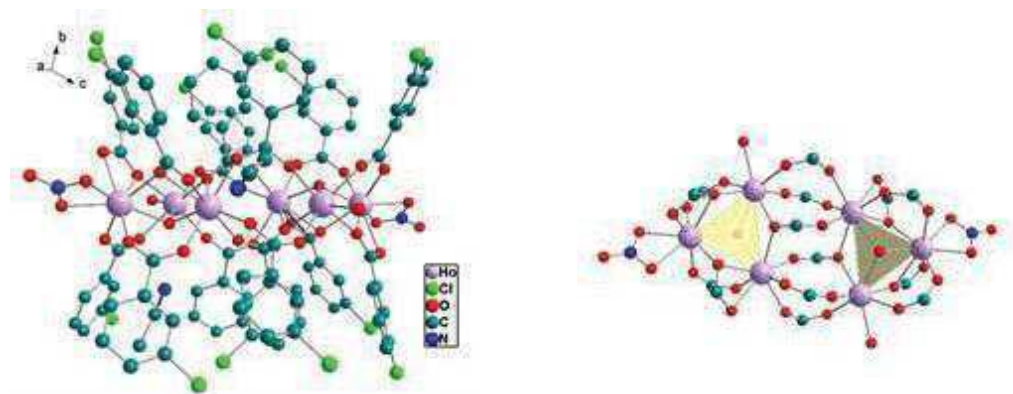


Fig.1 Molecular structure of hexa-lanthanide compound

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ELECTROCHEMICAL PROCESSES COUPLED TO A BIOLOGICAL TREATMENT FOR THE REMOVAL OF IODINATED COMPOUNDS

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Iodinated X-ray contrast media (ICM) compounds are one of the most widely used groups of hospital agents and have been extensively used for imaging of soft tissues [1]. They are a form of intravenous radiocontrast (radiographic dye) containing iodine, which enhances the visibility of vascular structures and organs during radiographic procedures. Some pathologies, such as cancer, have particularly improved visibility with iodinated contrast. They are usually applied at an average dose of 100 mL ICM at a concentration of 300 mg I/mL containing 30 g I and 60 g ICM; the overall use represents 1800 tonnes of iodine corresponding to 60 million doses worldwide per year [1,2]. When administered at high doses, they are rapidly eliminated *via* urine or feces. Because they are characterized by high hydrophilicity, they can be expected to be diluted in water rather than accumulated in organisms or to sediment solids [3]. Nowadays, the issue with the accumulation of ICM in the water body has received considerable critical attention since they are ubiquitously distributed in municipal wastewater effluents and in the aquatic environment and are not significantly eliminated by most biological sewage treatment processes [4].

Diatrizoate belongs to one of the typical ICM compounds. There are several methods available for the degradation of diatrizoate. Among these methods, electrochemical methods have significant advantages for the treatment of ICM, since they can selectively cut the carbon-iodine bonds that are often responsible of their biorecalcitrance. The recovery of iodine ions can be envisaged which can be particularly interesting to reduce the cost of the ICM production process. From this, the coupling of an electrochemical process and a biological treatment can be carried out to mineralize the organic part of the formed by-products, allowing the recovery of the iodide ions. Transition-metal macrocycles such as hematin, salcomine, phthalocyanines and vitamin B₁₂ have been examined extensively as catalysts for reductive dehalogenation of organohalides. Therefore, the degradation of diatrizoate, as a target compound, by an electrochemical reduction process, with or without the presence of a transition-metal catalyst, and the recovery of iodide ions is the purpose of this study.

Previous experimental work was performed, which mainly focused on cyclic voltammetry analyses of sodium diatrizoate and the examination of the catalytic activity of three different catalysts including salcomine, phthalocyanine and vitamin B₁₂ towards the reduction of sodium diatrizoate in different media. The results indicated that sodium diatrizoate can be directly reduced on glassy carbon electrode and salcomine showed a good catalytic activity. The low solubility of phthalocyanine did not allow the achievement of well-resolved voltammograms, but it seems that phthalocyanine also catalyzes the reduction of sodium diatrizoate. Regarding vitamin B₁₂, it did not catalyze the reduction of sodium diatrizoate at pH 7. Reductive electrolyses were then performed in a flow electrochemical cell to eliminate iodine from diatrizoate in the best operating conditions determined by electrochemical analysis.

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ELABORATION AND CHARACTERIZATION OF TI-BASED SUPERELASTIC FILMS

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Titanium (Ti) and its alloys currently serve for a large variety of applications in the aerospace, aeronautical and biomedical fields because of their excellent combination of high mechanical strength, low density and good corrosion resistance. Metastable β -type Ti alloys with superelastic behaviour and only composed of biocompatible elements (Nb, Ta, Zr, Sn) offer promising potentials especially for biomedical applications as cardiovascular stents, intravascular guidewires, embolization coils, orthodontic arch wires, orthopaedic staples and fixations,... which require a large variable geometry during operation and a constant force delivery over a long period in strain changing environments. There is considerable amount of investigations on the development of new Ti-based biocompatible alloys in the bulk form for their mechanical and superelastic performances, while very limited work exists on the superelastic nature of Ti-based alloy films. Superelastic thin films have enormous potentials for biomedical devices and micro-actuators systems.

This PhD work is focused on the relation between the structural properties of magnetron sputtered Ti-based films and their mechanical and superelastic behaviours in order to bring insights on the understanding of the martensitic phase transformation in small scale structures.

