JED3M
BREST
2019

De la molécule aux matériaux

3ème édition

LIVRE DES RÉSUMÉS

Mardi 19 Février 2019 de 8h30 à 17h à l'UFR de Sciences et Techniques de Brest

Partenaires

UBO Université de Bretagne Occidentale

CEMCA

SCF Société Chimique de France

UNIVERSITE BRETAGNE LOIRE / MATIERE MOLECULES ET MATERIAUX

THALES

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DÉPARTEMENT CHIMIE Faculté des Sciences et Techniques

Société Française de Physique

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Speakers Presentations

Created in 2007 by fisheries engineer Gildas Bodilis, Isi-Fish based in the port of Concarneau, Brittany is today the leader in buoy instrumentation for French tuna fishing.This company is known for its knowledge in the field of state-of-the-art information systems to help commercial fishing and ocean observation.

Thales is a world leader in high-technology specialized in aerospace, transportation, defense and security. Spread all over the world, including Brest, Thales offers a unique opportunity to create and deploy their surveillance and combat radar development components, as well as intelligence systems.

Founded in 1873, the *Société Française de Physique* (SFP) is an association of public utility whose mission is to develop and promote physics in France, by associating physicists of our country with its action. It creates the link between physicists and offers them different means of action. The actors and members of the SFP are volunteers, researchers, professors and members of physic labs, all of whom share the same passion for physics and its promotion in society.

The *Société Chimique de France* (SCF) is a non-profit association of public utility, founded in 1857. The SCF aims to bring together all persons whatever their sectors of activity (public or private bodies) concerned by chemistry sciences and their applications, to represent the interests of chemists and to promote the role of the chemical sciences.

After having followed the preparatory course at the *École Nationale Supérieure de Chimie* of Rennes, and spent a year studying *Sciences de la Matière* at the University of Rennes, Dr. Aurore Fraix enrolled at the *IUP Chimie et Biologie* of Nantes. In 2010, she finished a PhD in chemistry at the University of Brest. In 2011, she won a Marie-Curie fellowship to join Pr. Sortino's group as a research fellow. She has been a research assistant since 2017. Her current research focuses on the synthesis of molecules for multimodal therapy.

Oral Communications

Luminescent Lanthanide Multi-functional Switches

AL SABEA Hassan,[a] **MAURY Olivier,**[b] **RIOBE Francois,**[b] **BUCHER Christophe,**[b]
NOREL Lucie,[a,*] **RIGAUT Stephane**[a,*]

[a] **Institut des Sciences Chimiques de Rennes, UMR 6226, CNRS - Université de Rennes 1 - 35042 Rennes, France**

[b] **Laboratoire de Chimie, UMR 5182, CNRS - Ecole Normale Supérieure de Lyon, 46 allée d'italie, 69007 Lyon, France**

Email: hassan.alsabea@univ-rennes1.fr

Lanthanide ion complexes display unique long lived and narrow bandwidth luminescence ranging from the visible up to the near infra-red spectral range, with high emission efficiency, and a large (pseudo)-Stokes shift.[1] Therefore, switching lanthanide luminescence is of interest in the developing field of molecular switches.

Ruthenium(II) acetylide complexes are relevant redox active moieties as they promote a very efficient communication between carbon chains and the metal atoms. They can be incorporated in 4d-4f bmetallic complexes to achieve excellent redox-switching behavior for the ON/OFF switching of NIR emission in the case of Ytterbium(III).[2a-2b]

On the other hand, photochromic ligands, such as dithienylethenes, are easily inconverted between two isomers with different electronic structures and they are ideal optically triggered candidates for switching luminescence.[3]

In this work, we combine, for the first time, a newly modified dithienylethene (DTE) photochrome and a redox active metal complex with lanthanide ions to achieve switching of luminescence with two types of orthogonal stimuli: light and redox potential.

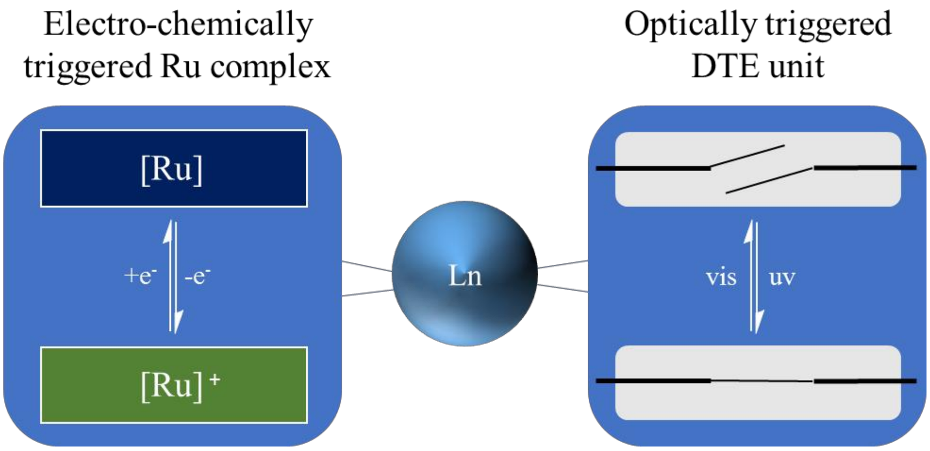

Figure 1. Concept of Ln Complex containing both electrochemically and optically triggered moities.

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[2] a) E. Di Piazza, L. Norel, K. Costuas, A. Bourdolle, O. Maury, S. Rigaut *J. Am. Chem. Soc.* **2011**, *133*, 6174, b) L. Norel, E. Di Piazza, M. Feng, A. Vacher, X. He, T. Roisnel, O. Maury, S. Rigaut *Organomet.* **2014**, *33*, 4824

[3] X. He, L. Norel, Y.-M. Hervault, R. Metivier, A. D'Aleo, Anthony, O. Maury, S. Rigaut *Inorg. Chem.* **2016**, *55*, 12635

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

M. Ciancone[1], K. Mebrouk[1], N. Bellec[1], C. Le Goff-Gaillard[2], Y. Arlot-Bonnemains[2], T. Benvegnu [c], M. Fourmigué[1], S. Cammas-Marion[1] and F. Camerel[1]

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

[2]Université Rennes 1, UMR-CNRS 6290, IGDR, BIOSIT, F-35000 Rennes, France
**e-mail: mathieu.ciancone@univ-rennes1.fr*

Metal-bis(dithiolène) complexes have proven being thermally stable and show a large absorption in near infrared with a high extinction coefficient (30 000 $M^{-1}.cm^{-1}$) [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 synthetize 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 $\mu g.mL^{-1}$. 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.

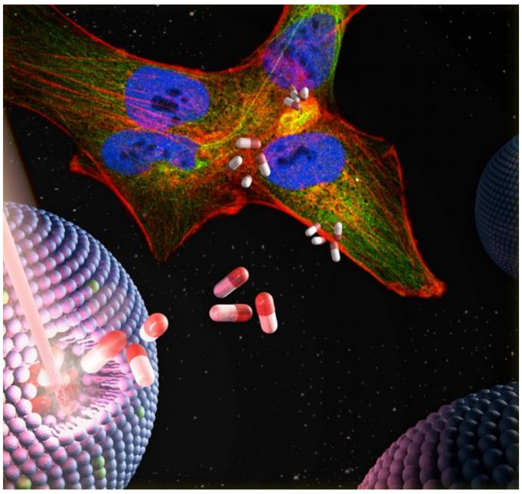

Figure: Illustration showing the release af active pharmaceutical ingredient toward tumor cells after liposome laser irradiation [4].

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[2] K. Mebrouk, F. Chotard, C. L. Goff-Gaillard, Y. Arlot-Bonnemains, M. Fourmigué and F. Camerel, Chem Commun, 2015, 51, 5268–5270.
[3] M. Ciancone and F. Camerel, Chem Commun, 2017, 53, 6339–6342.
[4] K. Mebrouk, M. Ciancone, T. Vives, S. Cammas-Marion, T. Benvegnu, C. Le Goff-Gaillard, Y. Arlot-Bonnemains, M. Fourmigué and F. Camerel, ChemMedChem, 2017, 12, 1753–1758.
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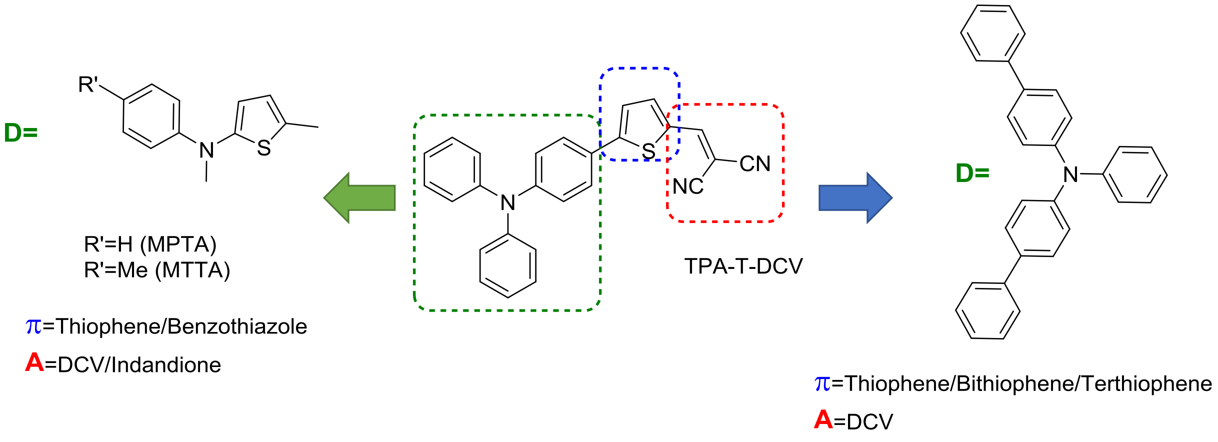
Donor-acceptor molecules with tailored properties as donor materials for Organic Solar Cells

J.M. Andrés Castán[1], **P. Simón Marqués**[1], **P. Josse**[1], **M. Blais**[1], **A. Habibi**[1], **C. Cabanetos**[1], **P. Blanchard**[1]

[1]MOLTECH-Anjou, UMR CNRS 6200, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France
** josemaria.andrescastan@univ-angers.fr*

The conversion of solar energy into electricity using solar cells is a renewable alternative to fossil fuels. Nowadays, organic solar cells (OSCs) have received increasing attention due to their advantages in comparison to silicon-based solar cells, such as lower manufacturing cost, lightweight and flexibility. They are usually composed by an active layer (made of an electron-donor and an electron-acceptor) placed between a transparent electrode with high work function and a low work function metallic electrode. In an attempt to improve their final performance, they have been subjected to constant modifications, such as variations of their architecture or development of new materials.

In the case of electron-donor materials, push-pull molecules have been widely used due to their good performance. Among others, triphenylamine (TPA) derivatives stand out due to strong electron-donor properties and high hole-mobility.[1] In addition, this structure is quite tunable since its modification can deeply affect the optical, electrochemical and photovoltaic properties.[2, 3] Regarding this fact, we present two different approaches to modify this structure. The first one is related to units with better electron-donating capability, i.e., *N*-methyl-*N*-phenylthiophen-2-amine (MPTA) and *N*-methyl-*N*-(p-tolyl)thiophen-2-amine (MTTA) (Fig. 1.a.). The second approach is related to a donor unit that usually provides better solubility and hole-mobility, i.e., *N*,*N*-bis(4-biphenylyl)aniline (Fig. 1.b). All of them will be combined with different π-spacers and accepting blocks to study their influence on the final properties of the push-pull systems, which will be further assessed as donor materials in OSCs.



a) b)

Fig.1. General structure of the synthesized push-pull molecules.

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Understanding elastically driven cooperativity in molecular photomagnetic materials

<u>A. Volte</u>[1], C. Mariette[1], M.-L. Boillot[2], M. Cammarata[1], B. Corraze[3], R. Bertoni[1], E. Collet[1], H. Cailleau[1], M. Lorenc[1]
[1]IPR UMR 6251, Rennes, France, [2]ICMMO UMR 8182, Orsay, France, [3]IMN UMR 6502, Nantes, France
**e-mail: alix.volte@univ-rennes1.fr*

Materials can be controlled via physical parameters like pressure or temperature. With the advent of ultrashort lasers pulses (typically femtosecond), light excitation has been added to the panel of available techniques for materials control. Two of the major aspects in so-called photo-induced phase transitions are reversibility, meaning the ability to switch back and forth between two states, and efficiency, corresponding to the ratio of the amount of transformed material on the quantity of provided light.

One possible approach to amplify the photoresponse is based on the material elastic properties. This was demonstrated for a light-sensitive and volume-changing Spin Crossover (SCO) material [1], meaning, a molecular crystal in which the unit cell is built with SCO molecule(s). In this molecule, the ligand field result in a splitting of the 3d levels of the metal ion (FeIII) into low energy and high energy ones. The population of high energy levels (at high temperature) changes the spin state and is accompanied by strong changes in Fe-ligand distances (and thus unit cell volume).

The sudden generation (via a laser pulse) of a high enough fraction of photo-excited molecules (switched from Low spin to High spin state) creates local negative pressure. This drives lattice expansion that can induce additional switching of neighboring molecules through positive feedback effect. This cooperative effect is associated as expected with a well-defined threshold mechanism.

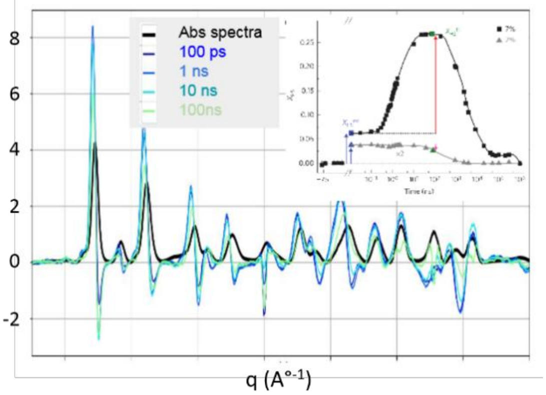

Figure *X-ray diffraction pattern and difference signal from reference of a powder SCO compound ; corresponding photoinduced transition dynamics obtained from optical experiment (insert)*

To unambiguously discriminate between spin state conversion and volume change, we performed Xray time-resolved diffraction study at synchrotron ESRF. The diffraction patterns measured from ps to µs time delays on nanocrystals powder films give a direct signature of the ultrafast volume expansion. Quantitative analysis of the powder spectra at ps time scale allows going deeper into the understanding of the cooperative aspects of the photo-induced spin conversion in these molecular materials.

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OB4

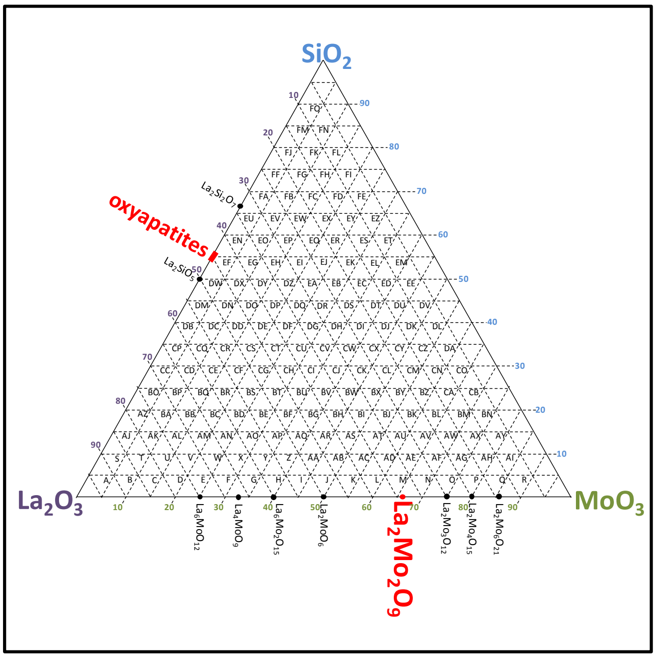
New lanthanum and molybdenum silicates for potential application as SOFC electrolyte

A. Pautonnier[1], M. Barré[1], S. Coste[1], P. Lacorre[1]

[1]Institut des Molécules et Matériaux du Mans, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9
**e-mail: antoine.pautonnier.etu@univ-lemans.fr*

In the current environmental context, producing clean energy by using renewable methods is particularly important. Developing the use of hydrogen and improving fuel cells efficiency is one way to reach this aim. Among the existing fuel cells, the solid oxide ones (SOFC) rely on an electrolyte with really good oxide ions conductivity. Unfortunately, the vast majority of good anionic conductors operate at very high temperatures such as around 800°C which lead to a premature aging of the devices and reduce the choice of materials for interconnection. In a project to generalize their use, these operating temperatures have to be lowered which implies the development of new oxide ions conductors.

In this objective, many compounds have been considered. Among them, there are lanthanum silicates such as the oxyapatite-type $La_{10}(SiO_2)_6O_3$ studied by Nakayama *et al* in 1995 **[1]**. In 2004, León-Reina *et al* pointed out that it was part of a conducting solid solution **[2]**. There are also lanthanum molybdates such as the compound $La_2Mo_2O_9$ studied by Lacorre *et al* in 2000 **[3]**. Despite their really good ionic conduction properties, 1.4×10^{-3} $S.cm^{-1}$ at 700°C and 6×10^{-2} $S.cm^{-1}$ at 800°C respectively, these two compounds have drawbacks which limit their use as electrolyte. Actually, the high synthesis and sintering temperatures of the oxyapatite-type solid solution coupled with its unidirectional conductivity lead to many difficulties during its production. Meanwhile, the compound $La_2Mo_2O_9$ is vulnerable to reduction and becomes the mixed conductor $La_7Mo_7O_{30}$ in a reductive atmosphere **[4]**. Due to the presence of dihydrogen at the interface between the anode and the electrolyte in a SOFC, the cell has however to operate in such an atmosphere. Using the compound $La_2Mo_2O_9$ as electrolyte could then lead to its reduction and eventually to short circuit problems.



In this context, looking for new compounds exhibiting a synergy of the advantages of the above phases but, at the same time, excluding their drawbacks is an interesting project. These two compounds are both included in the same ternary phase diagram: La_2O_3 – MoO_3 – SiO_2 which was never studied before. The final aim would be to find a new phase with an interesting conductivity at low temperature in the three space directions. This compound should, also, be easy to shape and sinter.

X-ray diffraction has been used to evidence phase diagram regions with new phases inside. The different synthesis techniques used in this project, the regions of interest in the phase diagram as well as a new defined compound will be presented in this communication.

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[1] S. Nakayama, T. Kageyama, H. Aono, Y. Sadaoka, *Journal of Materials Chemistry 5*, **1995**, 1801-1805.
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OB5

PLASMONIC NANOCRYSTALS SYNTHESIS: CONTROL OF THE MORPHOLOGY

J. Chrun[1], C. Vancaeyzeele[2], P.-H. Aubert[2], F. Vidal[2], L. Dupont[1]

[1]IMT Atlantique, 655 Avenue du Technopôle, 29280 Plouzané, [2]Laboratoire de Physico-chimie des Polymères et des Interfaces, 5 mail Gay Lussac 95031 Neuville sur Oise
**e-mail: jonathan.chrun@imt-atlantique.fr*

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 wave-lengths 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 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 X-Ray Diffraction (XRD).

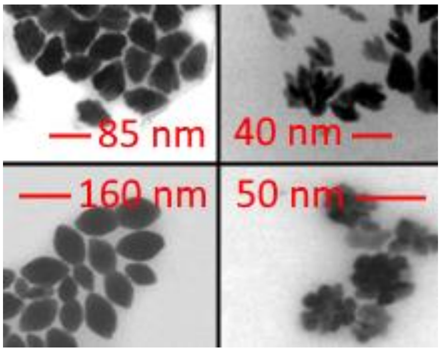
a $Zn(L_1)_2 + 2\ R_2\text{-}OH \longrightarrow Zn(OH)_2 + 2\ L_1\text{-}R_2$

b $Al(L_2)_3 + 3\ R_2\text{-}OH \longrightarrow Al(OH)_3 + 3\ L_2\text{-}R_2$

c $x\ Zn(OH)_2 + y\ Al(OH)_3 \longrightarrow Al{:}ZnO + z\ H_2O$

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

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.



Scheme 2 TEM of obtained AZO NCs

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Acknowledgments

This research was supported by a DGA grant to the Institut Mines-Télécom Atlantique
This work has been realized by the facilities of the Plateforme Microscopies & Analyses, Federation I-Mat (FR4122) of the University of Cergy-Pontoise (France)
The purchase of SEM/Raman was partially supported by the Ile-de-France Region through the Sesame project.

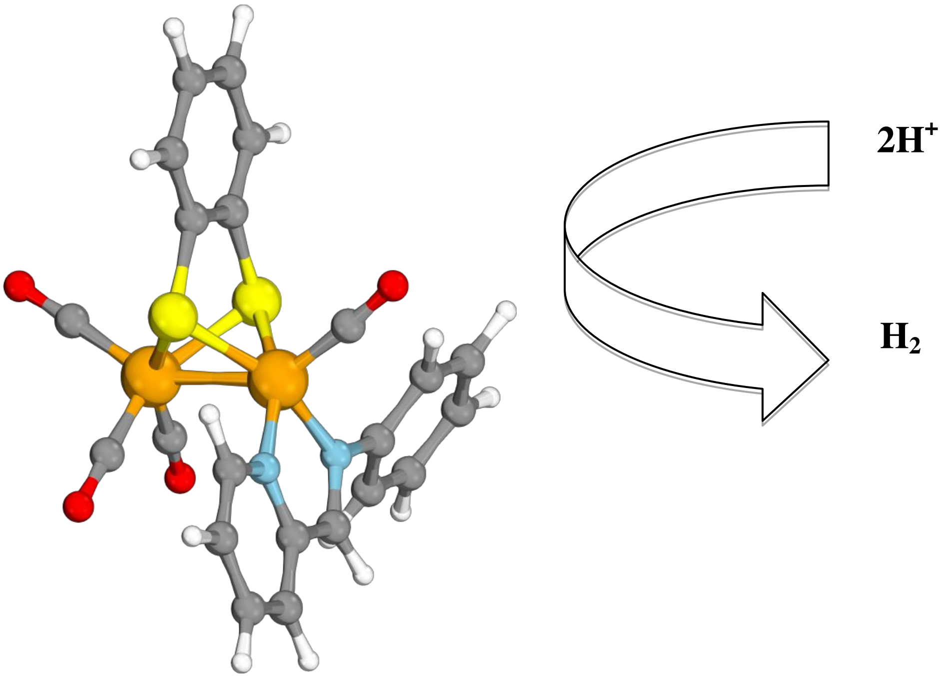
Bioinspired mimics of [FeFe]hydrogenases for H_2 generation using a non innocent redox ligand

A. Mele[1], F. Arrigoni[2], C. Elleouet[1], P. Schollhammer[1], G. Zampella[2]

[1] UMR CNRS 6521 "Chimie, Electrochimie Moléculaires et Chimie Analytique" Université de Bretagne Occidentale, UFR Sciences et Techniques 6 Avenue Victor Le Gorgeu, 29200 Brest (France)
[2] Department of Biotechnology and Bioscience, University of Milano – Bicocca, Piazza della Scienza 2, 20126 Milan (Italy)

**e-mail:* andrea.mele@univ-brest.fr

Since the discovery of [FeFe] hydrogenases, several mimics of their active site, the H-cluster, have been synthesized to understand the functioning at the molecular level and in order to design efficient catalysts for the H^+/H_2 conversion.[1]
In this communication will be presented the synthesis of a novel complex $[Fe_2(CO)_4(\square^2$-(pyridylmethylene)aniline)(μ-benzene-1,2-bis(thiolate))] able to electrocatalyze the production of hydrogen using a weak acid and a detailed mechanism will be postulated from cyclic voltammetry and DFT calculations.
It will be shown how the use of a non-innocent redox ligand can influence the reactivity of the complex and its importance on the catalytic activity.[2][3]



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CARBOHYDRATES ELECTROGRAFTED ON GLASSY CARBON SURFACE FOR ANTIFOULING COATINGS

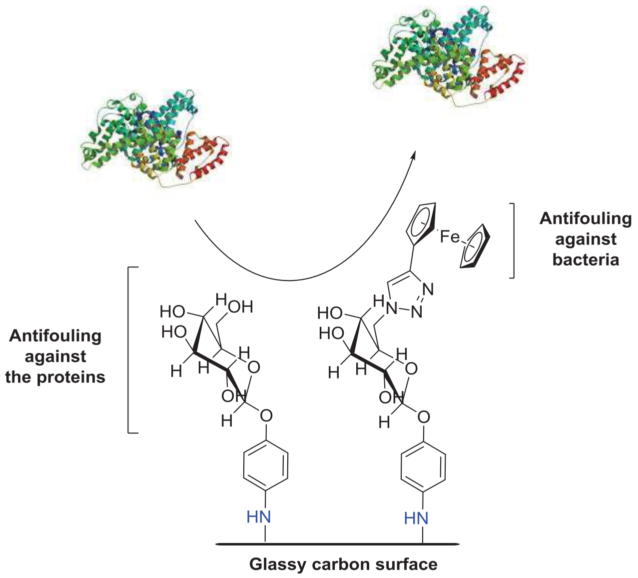
Fanny PEIGNEGUY[1], Sylvie DABOS SEIGNON[1], Magali ALLAIN[1], Christine BRESSY[2], Charles COUGNON[1], Frédéric GOHIER[1]

[1] Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers cedex, France
[2] Université de Toulon, Laboratoire MAtériaux Polymères-Interfaces-Environnement Marin (EA 4323 MAPIEM) CS 60584 -83041 Toulon cedex 9, France
**e-mail: fanny.peigneguy@etud.univ-angers.fr*

Marine fouling is a phenomenon that takes place when a surface is immersed in seawater. Thousands of marine organisms as bacteria, barnacles, algae settle on the surface causing environmental, economic and material issues [1]. Some coatings have been developed in the sixties from tributyl tin (TBT) used as a biocide in self-polishing paints but the leaching of this biocide in the environment is very toxic and its use was prohibited in 2008. To avoid these problems, research focuses more and more on coatings able to repel microorganisms and all the fouling chain without any leaching in seawater functionalizing on the surface polymers as poly(ethylene glycol) (PEG), zwitterionic polymers, self-assembled monolayers (SAMs), enzymes [2]...

So, the research group of E.M.Scanlan have demonstrated that carbohydrates grafted by reduction of diazonium salts were able to prevent the adhesion of proteins on surface [3]. Indeed, the hydroxyl groups present on the carbohydrates stimulate the hydrogen bonds with molecules of water, which create a "water barrier" able to prevent the formation of the conditioning film. Moreover, our group has already shown that polyacrylates bearing linear conjugated systems can operate against bacteria's colonization applying low electrical potentials to modify surface polarity [4]. Indeed, bacteria are unable to settle on surface whose polarity changes constantly. So, the goal of the project is to immobilize carbohydrates linked to an electrostimulable-conjugated systems able to repulse both proteins and bacteria thank to their redox properties.

First, we focused on the grafting of 4-aminophenyl-β-D-glucopyranoside on glassy carbon and PPF surfaces by amine oxidation in acetonitrile solution [5]. Then, this grafting has been analysed by cyclic voltammetry, XPS, AFM and water contact angle experiments. We also studied the controlled cleavage of carbohydrates by oxidation of anomeric position. Secondly, we synthesized ferrocene derivatives and functionalized surface in acetonitrile or seawater. Then, we studied the stability of the layer electrochemically before testing these graftings in biological solution in presence of proteins then bacteria.



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

M. Fernandez[1], A. Urvoas[2], M. Valerio-Lepiniec[2], A. Burel[3], P. Minard[2], E. Durjardin[4], P. Even-Hernandez[1] and V. Marchi*[1]

[1]Institut des Sciences Chimiques de Rennes, University Rennes 1, CNRS : UMR 6226, Rennes, France, [2]Institut de Biologie Intégrative de la Cellule, CNRS : UMR 9198, CEA : DRF/I2BC, Université Paris-Sud - Paris 11, Orsay, France, [3]Biosit: Biologie, Santé et Innovation Technologique CNRS : UMS 3480, INSERM, Rennes, France, [4]Centre d'élaboration de matériaux et d'études structurales, CNRS : UPR 8011, INSA Toulouse, Université Paul Sabatier - Toulouse 3, Toulouse, France

**valerie.marchi@univ-rennes1.fr*

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. In this context, assemblies of gold nanoparticles were designed using artificial repeat αRep protein pairs of high affinity exhibiting a dissociation constant in the nanomolar range.[1,2] These promising proteins induce the self-assembly of complementary colloids in a controlled manner, whilst providing a control on the interparticle distance.

Here we present the design of αRep proteins driven self-assemblies of semiconductor nanoparticles (Quantum dots, QDs) and gold nanoparticles (nPAu). First, fonctionnalization of QDs and nPAu is achieved exchanging an initial polycystein peptidic ligands at the surface of the NP with the αRep proteins.[3] The efficiency of the protein grafting was demonstrated by agarose gel electrophoresis. The molecular recognition properties of the protein-functionalized nanoparticles are evidenced using Surface Plasmon Resonance technique. The selective formation of large colloidal assemblies (Figure 1) of complementary nanoparticles is demonstrated by transmission electronic microscopy and finally characterized by fluorescence spectroscopy. These results open the route to the design of hybrid colloidal assemblies with original optical response.

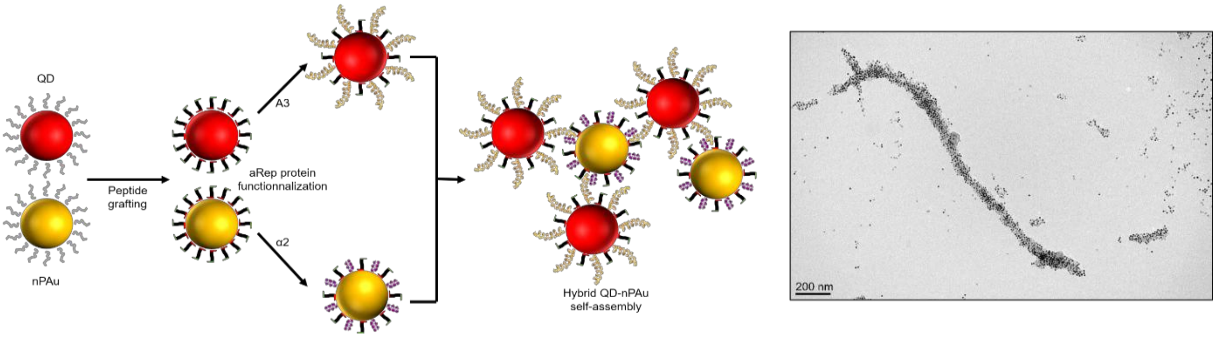

Figure 1: Schematic representation of the three steps process of production of hybrid self-assemblies (left) and TEM image of self-assembled QDs and nPAu (right).

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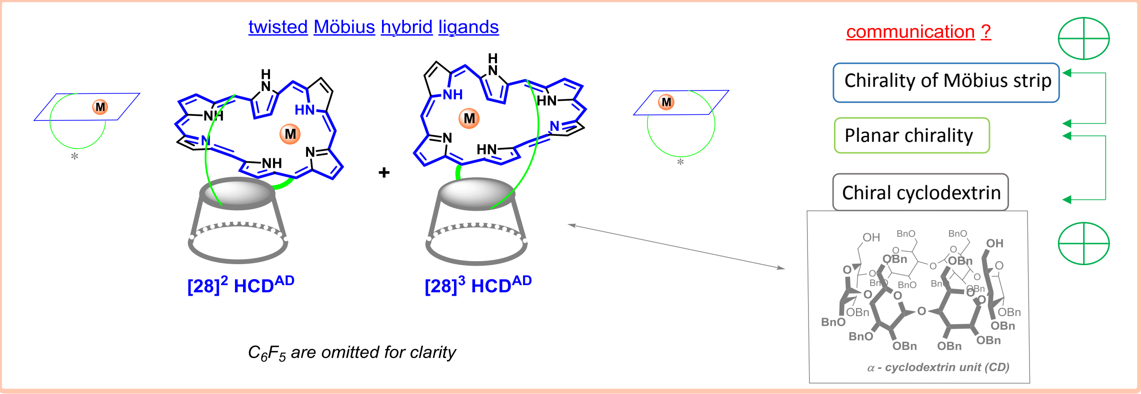
DEMYSTIFYING CHIRALITY INDUCTION IN MÖBIUS HEXAPHYRIN-CYCLODEXTRIN METAL COMPLEXES

R. Benchouaia[1], N. Cissé[1], B. Boitrel[1], M. Menand[2], S. Le Gac[1]

1 Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université Rennes 1, 263 avenue du Général Leclerc, 35042 Rennes cedex, France
2 Sorbonne Université, UPMC Univ Paris 06, CNRS, Institut Parisien de Chimie Moléculaire (IPCM), UMR 8232, 4 place Jussieu, 75005 Paris (France)
E-mail: ragaa.benchouaia@univ-rennes1.fr

Expanded porphyrins are macrocyclic compounds with more than 4 pyrrole rings offering several applications. Hexaphyrins [1] (6 pyrrole rings) present different types of aromaticity and conformation 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 functionnal groups) but paradoxically, the induction of chirality in Möbius rings is still in its infancy. Indeed, macrocycles that have a Möbius conformation are intrinsically chiral and the control of their chirality is important to understand their properties. Limited examples of enantiomeric separation of Möbius rings have been achieved and only one asymmetric synthesis[3,4a] is accomplished.

In our lab, we thus explore the coordination and chiroptical properties of capped hexaphyrins.[4] 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 planar or twisted, and capped by one cyclodextrin with 2 linkages (Scheme 1). Interestingly, these hybrids ligands present 3 sources of chirality : at the level of the Möbius strip, the planar chirality due to the linkage and the intrinsic chirality of the cyclodextrin unit. Coordination and chiroptical studies reveal a chiral induction with the highest stereoselectivity reported to date for one Möbius ring (up to 80% d.e.). The demystification of this chirality induction is assignable to communication between the 3 sources of chirality. Ultimately, these hybrid ligands would lead to allosteric receptors and catalysts,[5-6] which is the concern of our researches.



Scheme 1 : Representation of Möbius hexaphyrin-cyclodextrin complexes

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

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SHOCK INDUCED PHASE TRANSITION

Y. CHERNUKHA[1]*, M. SERVOL[2], M. LORENC[2], T. PEZERIL[3]

[1]Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans Université, 72085 Le Mans,
[2]Institut de Physique de Rennes, UMR UR1-CNRS 6251, Université de Rennes 1, F-35000 Rennes,
[3]Chemistry Department, MIT, Cambridge, Massachusetts 02139, USA.

**e-mail: yevheniia.chernukha.etu@univ-lemans.fr*

Shock waves in condensed matter are of great importance for many areas of science and technology such as hypervelocity launchers, synthesis of new materials, production of high-temperature and high-density plasma fields [1], applications in controlled thermonuclear fusion [2], and a variety of medical therapies [3].

Shock wave focusing is visualized at the micron scale in an all-optical single-shot experiment [4]. The optical set-up includes an axicon that focuses an intense laser picosecond excitation pulse into a ring-shaped pattern at the surface of different bi-stable materials (such as V_2O_3 thin films [5], $[Fe(NH_2\text{-}trz)_3](Br)_2$ nanoparticles in liquid suspension [6], T_3O_5 pressed powder[7]). Optical excitation generates a surface acoustic wave that propagates in the plane of the sample and converges toward the center (Fig.1.)

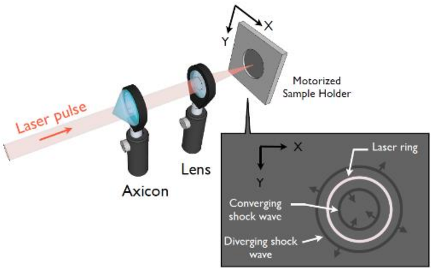

Fig.1. Shock wave generation principle

A series of images taken with a femtosecond probe pulse at variable delays are used to follow the shock propagation toward the center. Converging shock waves create a high pressure point at the center of the ring where they acoustically focus. With this technique, we can spatially separate the laser-induced and the shock-induced transformation/transition.

Throughout this 2D shock focusing technique we can determine the role of the shock wave during the transformation/transition process. The ultimate goal is to reveal whether or not laser generated strain waves can alone drive the phase transition in a transient/ permanent regime. The latter case is tested with post-mortem Raman imaging.

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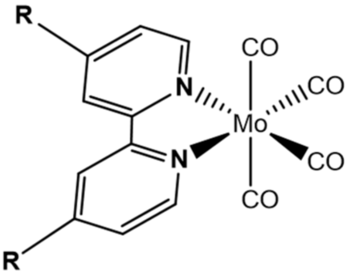
Synthesis and characterization with spectroelectrochemistry of transition metal catalysts for CO_2 electroreduction

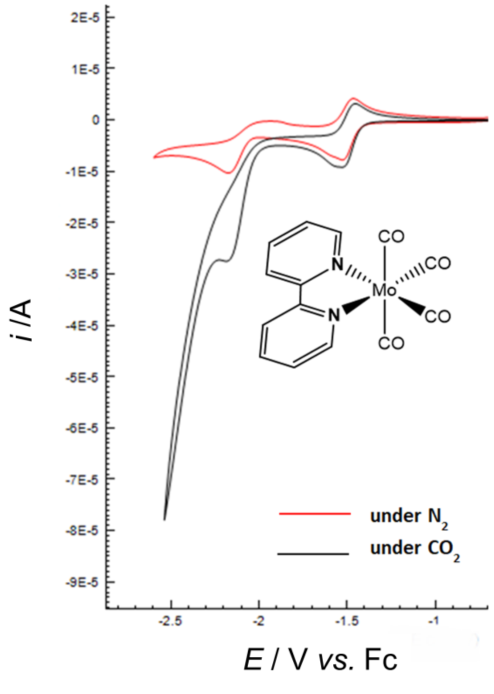
Carlos Garcia Bellido[a], **Nolwenn Cabon**[a], **Nicolas Le Poul** [a],**Frédéric Gloaguen**[a*]

[a] *Laboratoire CEMCA, UMR 6521 CNRS, Université de Brest, CS 93837, 6 avenue Le Gorgeu,*
29238 Brest, France
** e-mail : Frederic.Gloaguen@univ-brest.fr*

In the recent years, significant progress has been performed to develop efficient and low-cost homogeneous molecular electrocatalysts for CO_2 reduction. Many metal complexes based on Mn[1] or Ni[2] have shown promising electrocatalytic properties since they display relatively low overpotential values, good activity and good selectivity. However, the catalytic pathways remain poorly understood. Molybdenum and tungsten carbonyl complexes bearing a bipyridine ligand have recently attracted attention since these complexes can perform the catalytic reduction of CO_2 upon electrochemical input[3], showing that the presence of the bipyridine ligand is essential for the catalysis. For instance, enhancement of the catalytic properties was obtained by incorporation of electron-donating groups, such as tBu, on the pyridine ring.[3] In that context, we have developed new $[Mo(CO)_4(bpy\text{-}R_2)]$ complexes (R = H, tBu, NO_2, CO_2H, see Figure below), focusing our efforts on the modulation of the electronic properties of the system by variation of the substituting group R on the pyridine ring. The objective of this work is to obtain new electrocatalysts and to correlate electrochemical and spectroscopic results to computational ones in order to achieve a better understanding on the mechanism followed by these systems.



R = H (**1a**), tBu (**1b**), NO_2 (**1c**), COOH (**1d**)



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AUTONOMOUS RF SENSORS INTERROGABLE BY MARINE DRONES FOR INFRASTRUCTURE MONITORING

K.Bouzaffour[1], F.Gallée[2], P.Talbot[1], B.Lescop[1], S.Rioual[1]

[1] Lab-STICC,UMR CNRS 6285,Université de Bretagne Occidentale,6 av. Le Gorgeu, Brest Cedex, France
[2] Lab-STICC/MOM, Telecom Bretagne, Technopôle Brest-Iroise, CS 83818, 29238 Brest Cedex, France

Corrosion of reinforced concrete structures is one of the major concerns in the field of durability and serviceability of buildings and constructions. In marine environment, the degradation process is initiated by chloride penetration and leads subsequently to steel depassivation. Fig. 1 displays an example of degradation of such reinforced concrete infrastructure. Although several off line procedures are currently available for the detection of corrosion, no application allows the non-destructive detection of chlorides and the monitoring of the chemical state of steel. Within this context, as shown in Fig. 2, the aim of the present work is the development of a sensor sensitive to degradation of steel embedded in the infrastructure, here a marine wind turbine, and which can be remotely interrogated by a marine drone.

Fig.1. The effects of chloride on reinforced concrete

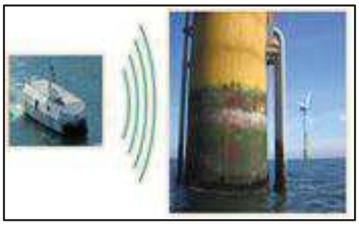

Fig.2. Drone interrogating a sensor embedded in an infrastructure

Following the previous studies performed in our group on corrosion sensors [1], several types of fully passive autonomous solutions will be considered during the phD. One of them is inspired from the chipless RFID architecture which involved radiofrequency resonators sensitive to the chemical and physical changes of the material under investigation. To develop such device, radiofrequency characterization including dielectric characterization of materials are mandatory. Preliminary results will be presented at the conference.

Acknowledgement
This work was supported by the European Union through the European Regional Development Fund (ERDF), the Ministry of Higher Education and Research, the Région Bretagne, the Conseil général du Finistère and Brest Métropole Océane, through the CPER Project 2015–2020 MATECOM. One of the authors (KB) acknowledges the Région Bretagne for a financial support through the SAMM program.

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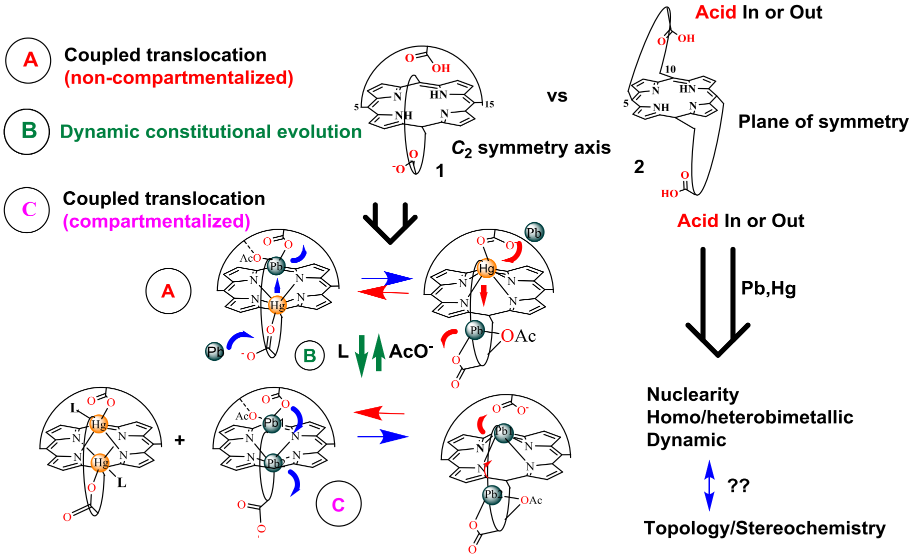
OC6

SUPRAMOLECULAR COORDINATION CHEMISTRY WITH BIS-STRAPPED PORPHYRIN LIGANDS.

W. BARAKAT[1], S. LE GAC[1], I. HIJAZI[2], B. BOITREL[1]

[1]Institut des Sciences Chimiques de Rennes, UMR CNRS 6226,
Université de Rennes 1, 35042 Rennes Cedex, France.
[2]Plateforme de Recherche et d'Analyse en Sciences de l'Environnement, Campus Universitaire de Rafic Hariri – Hadath (Liban)
E-mail: wael.barakat@univ-rennes1.fr

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 Bi(III), Hg(II) and Pb(II) has been investigated and compared to **1**.



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CIRCULARLY POLARIZED LUMINESCENCE OF NOVEL CHIRAL HELICENE MOLECULES

Kais Dhbaibi,*[1,2,3] Ludovic Favereau,[1] Bassem Jamoussi,[3] Jeanne Crassous.[1]

Univ Rennes, CNRS, ISCR-UMR 6226, 35000 Rennes, France.[1]
University of Gabès, Faculty of Science of Gabès, Zrig, 6072 Gabès, Tunisia.[2]
Université Virtuelle de Tunis, UR17ES01 Didactique des Sciences Expérimentales et de Chimie Supramoléculaire, Tunis, Tunisia.[3]

kais.dhbaibi@univ-rennes.fr

Chirality describes an object that can exist as a pair of non-superimposable mirror-images. Despite its well-recognized role in biological functions, chirality remains underexplored in materials science area.[1] One of the most intriguing properties of chiral molecules is their ability to interact specifically with left- and right-handed circularly polarized light either in absorption (Electronic Circular Dichroism, ECD) or in emission (Circularly Polarized Luminescence, CPL). The latter is becoming a focal point in several applications, such as 3D displays, information storage and bioresponsive imaging.[2] Helicenes are polycyclic aromatic compounds with non planar screw-shaped skeletons formed by *ortho*-fused benzene or other aromatic rings,[3] and can be regarded as valuable inherently chiral building blocks exhibiting good CPL activity.[4] In this context, a new family of chiral push-pull helicene derivatives, in which different substituents with various electron donating and withdrawing groups are attached to the helicene core, were successfully synthesized (see **$H6(A)_2$ figure 1A**). The study of their polarized photoluminescence reveal strong and tunable CPL responses with high dissymmetry factors ($g_{lum} = \Delta I/I = 2 \times (I_L - I_R / I_L + I_R) > 10^{-2}$ at 430 nm) which present a huge increase in comparison with the simpler carbo[6]helicene reference **(H6)**. This result also correspond to one of the highest values of g_{lum} reported for the small organic molecules **(Figure 1B).**[5]

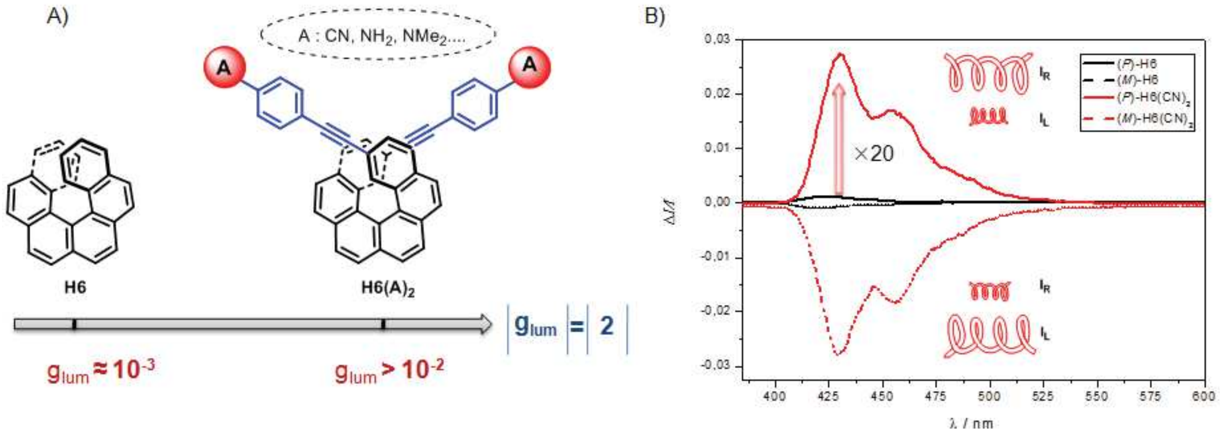

Figure 1 : A) Molecular structure of the studied helicene derivatives and their corresponding dissymmetry factor (g_{lum}). B) CPL spectra of enantiopure H6 and $H6(CN)_2$.

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High-power limitations of graphene nanocoated optical taper saturable absorbers

M. Kemel*[1], **P. Mouchel**[2], **G. Semaan**[1], **M. Salhi**[1], **M. Le Flohic**[2], **and F. Sanchez**

[1]Laboratoire de Photonique d'Angers, 2 Bd Lavoisier, 49045 Angers, France
[2]Lumibird, 2 rue Paul Sabatier, 22300 Lannion, France
**meriem.kemel@etud.univ-angers.fr*

In the last two decades, graphene has attracted much attention because of its unique properties. Particularly, thanks to its Saturable Absorption (SA) characteristics, graphene is widely used in mode-locked fiber lasers to produce ultra-short pulses. Different methods have been used to realize a graphene-based SA. In our case, we use a graphene nanocoated fiber tapers (GNOTs). It is fabricated by reducing a single mode fiber's diameter to approximately 20 µm over 5 mm of waist long. Graphene nano-flakes initially in suspension in water are then deposited on the taper waist thanks to the optical tweezers effect.

While graphene has demonstrated very good saturable absorption properties for low power, there are very few results concerning its use in high power fiber lasers. In this communication we point out the deterioration of the SA properties of the GNOTs under high input optical power [1]. Indeed, when a certain power is injected in a GNOT, its SA properties are irreversibly modified. Figure 1 shows the experimental setup.

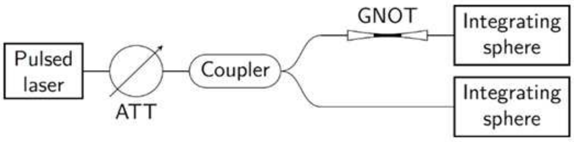

Figure 1: Power-dependent setup. ATT: variable attenuator. GNOT: graphene nanocoated optical taper.

The Pulsed laser, playing the role of the optical source, emits 5 ps pulses at a central wavelength of 1562 nm. The average power injected in the GNOT is controlled by the variable attenuator. Transmission over the time for different incident powers is measured. We notice that the GNOTs lose their SA properties as soon as the injected power is above a certain threshold. A temperature tests was also made in function of power. It has revealed that at high power the GNOTs reach very high temperature, which causes an irreversible damage of their properties.

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OD2

[4]Cyclo-9-ethyl-2,7-carbazole nanoring: Synthesis, characterization and application

Fabien Lucas,[a] **Cassandre Quinton,**[a] **Emmanuel Jacques,**[b] **Joëlle Rault-Berthelot,**[a] **Cyril Poriel**[a]
[a]*Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France*
[b]*IETR, Département Microelectronique & Microcapteurs UMR CNRS 6264, F-35000 Rennes, France*
E-mail: fabien.lucas@univ-rennes1.fr

Organic electronics (OE) has been an intense research field which deals with the design, the synthesis, the characterization and the use as active layer of organic semi-conductors (OSC) in different devices OE applications gather three main devices: Organic Light Emitted Diodes (OLED), Organic Field-Effect Transistors (OFET) and Organic Photovoltaic cells (OPV). For the last ten years our group has been developing OSCs targeting specific applications such as OLEDs and OFETs.[1-5]
Recently, new generations of OSCs have appeared in the literature: the nanorings. Thanks to pioneer works of Jasti, Itami and Yamago's groups,[6-9] nanorings have caught the attention of our group.
However, and despite the fantastic development of OE technologies in the last twenty years, only very few examples of nanorings incorporation in organic devices have been reported so far. Huang and co-workers have for example reported the incorporation of a 4-cyclofluorene as green emitter in an OLED.[10]
In order to further incorporate nanorings in efficient electronic devices in the future, precise knowledge of the charge carriers occuring in nanorings is a mandatory step. To the best of our knowledge, no example of nanoring in an OFET has been reported so far.
In the present work, we report the synthesis, the electronic properties and the incorporation in an OFET of a cyclic tetracarbazole namely [4]cyclo-*N*-ethyl-2,7-carbazole (**[4]C-Et-Cbz**). Thanks to its appealing properties (particularly its electron rich character), the carbazole fragment has been widely used in the design of functional materials for OE and appears therefore as an interesting building unit to construct nanorings. The first examples of cyclocarbazoles have been reported by Yamago *et al* in 2016.[7] Herein, we report an improved synthesis of a cyclocarbazole nanoring including four carbazole fragments possessing nitrogen atoms substituted with ethyl chains. The structural, electrochemical and photophysical properties will be detailed and rationalized thanks to molecular modelling. In addition, the electronic properties of [4]Cyclo-9-ethyl-2,7-carbazole ([4]C-EtCbz) will be compared to those of its homologues [4]Cyclo-9,9-diethyl-2,7-fluorene[11] ([4]C-diEtF) and [8]Cycloparaphenylene[9] ([8]CPP) (Figure 1) in order to determine the influence of i) the presence of a bridge between two phenyl units, and ii) the nature of this bridge. Incorporation of [4]C-EtCbz in an OFET will be finally presented. This work shows not only that nanorings can be successfully introduced as an active layer in an OFET but also provides a first benchmark for nanorings.

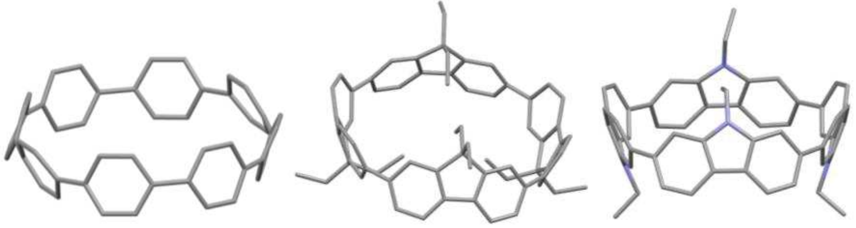

*Figure 1 X-ray structure of **8CPP**, **[4]C-diEtF** and **[4]C-EtCbz** (from left to right)*

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3-Dimensional conjugated systems with potential application in Organic Photovoltaics

<u>P. Simon Marqués</u>[1], J.M. Andrés Castán, C. Cabanetos[1], P. Blanchard[1]

[1]MOLTECH-Anjou, UMR CNRS 6200, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France
**e-mail: (pablo.simon@univ-angers.fr)*

In the framework of Organic Photovoltaics (OPV), the research has overwhelmingly focused on solution-processed conjugated polymer:fullerene blends.[1] More recently, small π-conjugated molecules have spread owing to their good photovoltaic performance as electron-donors[2] or electron-acceptors[3] combined with their good processability either in solution or by vacuum process. Regarding their chemical structure, 3-dimensional (3-D) molecules have received a particular attention due to their potential isotropic charge-transport properties, reduced crystallization and higher solubility than 2-D systems.

Here, we present the research and preparation of different group of 3-D molecules for their application in Organic Solar Cells, starting from the computational calculation, synthesis and characterization of the materials to their implementation in the photovoltaic devices. Being involved in the European project SEPOMO, we have the opportunity to collaborate with leading universities in photovoltaics, with whom we are able to study, material modelling, photophysic properties, surface analysis, etc, understanding the phenomena that take place in our materials. On the other hand, the participation of important enterprises like Heliatek GmbH brings a business point of view, strongly oriented to the processability and stability of compounds and devices.

Holding together academia and industry, ITN SEPOMO invests in training the next generation of photovoltaic researchers.

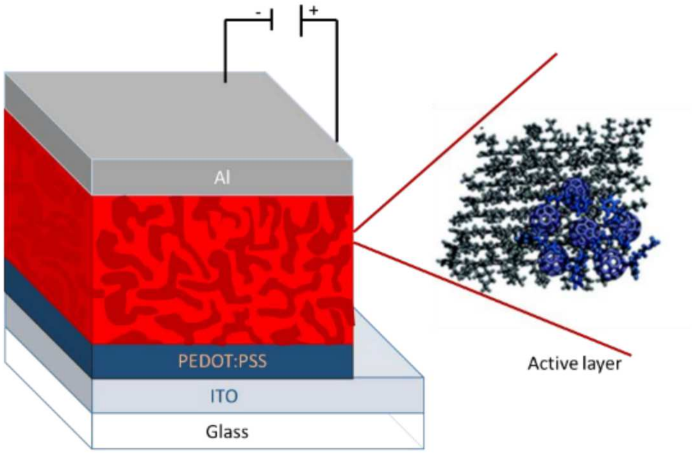

Figure1. BHJ solar cell structure.

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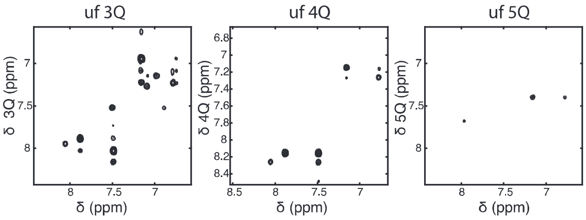
ULTRAFAST MULTIPLE QUANTUM AND DIFFUSION ORDERED NMR SPECTROSCOPY FOR MIXTURE ANALYSIS

C. Jacquemmoz[1,2], M. G. Concilio[2], J.-N. Dumez*[1,2]
[1] CEISAM, UMR-CNRS 6230, Université de Nantes, Nantes
[2] ICSN, CNRS UPR 2301, Université Paris Sud, Université Paris Saclay, Gif sur Yvette
**e-mail: (jeannicolas.dumez@cnrs.fr)*

Molecular structure elucidation is an important topic in numerous fields such as in pharmaceutical industry, metabolomics or for reaction monitoring. Frequently the molecules of interest are not alone: they are in a mixture leading to a more complex analysis. In this context, nuclear magnetic resonance (NMR) spectroscopy is a powerful tool as it is a non-destructive method that provides structural and quantitative information. Multidimensional NMR (ND NMR) can in particular bring a wealth of structural information. However ND NMR requires long experiment durations due to the need to record several sub-experiments to construct additional dimensions[1]. These long durations are a problem when samples evolve in time or if many samples have to be analyzed.

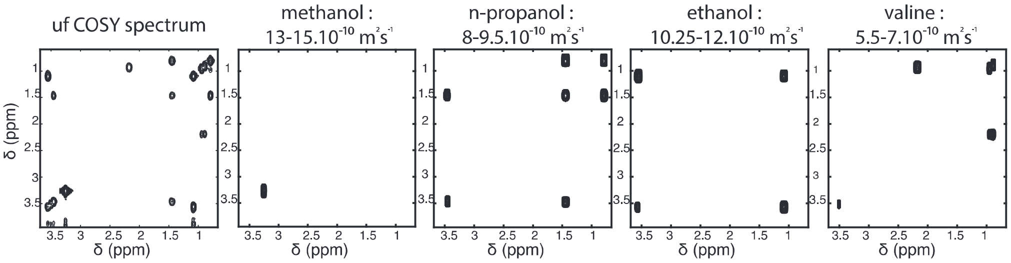
Different approaches have been proposed to accelerate ND NMR. The most efficient of these methods so far has been proposed by Lucio Frydman in 2002 and consists of spatially encoding the chemical shift dimension[2]. It has been successfully applied to reduce the time needed to record COSY[3], J-RES[4] or HSQC[3] spectra.

Here we show how this Spatial Encoding (SPEN) approach can been used to shorten two kinds of experiments that are very useful for mixture analysis: Multiple Quantum Spectroscopy (MQS) and Diffusion Ordered SpectroscopY (DOSY). MQS consists of the correlation of multiple quantum coherences to single quantum ones. It has been extensively used for the analysis of mixtures of polyaromatic compounds, such as phenolic antioxidant in olive oils or aromatic pollutants in fossil fuels… It was shown already that single and double quantum coherences can be encoded spatially, and here we prove that higher coherence orders can also be spatially encoded. Using this methodology, an example of a reaction monitoring is demonstrated[5].



Example of ultrafast 3Q, 4Q and 5Q spectra obtained on a mixture of phenol, anthracene and phenanthrene. Each spectrum has been obtained in less than 100 ms.

Another powerful NMR experiment for mixture analysis is DOSY. It is usually employed to separate signal originating from compounds of different sizes in a mixture, through the encoding of their translational diffusion coefficients. The 2D version of this experiment (that separates 1D NMR spectra) has been used in numerous fields but the 3D version (that separates 2D NMR spectra) suffers from the important experimental duration needed (from 3 hours to more than 14 hours). We show that the use of spatial encoding of the indirect chemical shift dimension can reduce the experimental time by more than one order of magnitude[6].



The two concepts, MQS and DOSY, are also combined with a spatially encoded MQS-DOSY experiment.

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OD5

Design of an Elliptical-Core Few-Mode Fiber for Mode-Independent Wavelength Conversion

Joseph Slim, **Mathilde Gay, Christophe Peucheret**

Univ Rennes, CNRS, FOTON – UMR 6082, F-22305 Lannion, France
joseph.slim@univ-rennes1.fr

While the main benefit of optical communications is to achieve high data transmission capacities, the processing of the data generally needs to be performed in the electrical domain, thus potentially requiring multiple optical-to-electrical-to-optical conversions. However, some processing functionalities such as wavelength conversion or regeneration could be performed more efficiently directly in the optical domain, as investigated in the field of all-optical signal processing (AOSP) [1].

Mode-division multiplexing (MDM) is currently being investigated as a mean to scale up the capacity of optical communication systems beyond the current limits of single-mode fibers [2]. Most of the research efforts have been so far dedicated to the demonstration of mode-multiplexing devices and point-to-point links. However, it is clear that MDM systems could also benefit from the implementation of AOSP functionalities. Parametric processes based on four-wave mixing (FWM) are particularly attractive for the wavelength conversion of complex optical signals exploiting the phase and amplitude dimensions (e.g. quadrature-amplitude modulation – QAM). Intermodal FWM has been investigated in a few-mode fiber (FMF) [3], and elliptical-core few-mode fiber (EC-FMF) [4]. In some scenarios, one may need to simultaneously wavelength-convert signals carried by all the modes supported by the transmission FMF. The use of photonic lanterns has been proposed to convert the MDM signals into single mode tributaries, followed by parallel single-mode wavelength conversions and single-to-multimode conversion [5]. The scheme is however cumbersome, and it would be beneficial to perform simultaneous multimode wavelength conversions in a single nonlinear medium for all the spatial modes of a FMF. This in fact appears to be quite challenging, because the phase matching condition needs to be satisfied for all the modes. However, mode-independent single pumped parametric amplifiers based on intramodal FWM has been investigated in a FMF [6] and EC-FMF [7], which enables many applications such as wavelength conversion and phase-sensitive amplification.

We show here the design of a nonlinear dispersion-shifted EC-FMF that provides small dispersion and high differential mode delay between the three modes LP_{01}, LP_{11a} and LP_{11b}, and allows simultaneous wavelength conversion for the three modes independently, based on intramodal FWM.

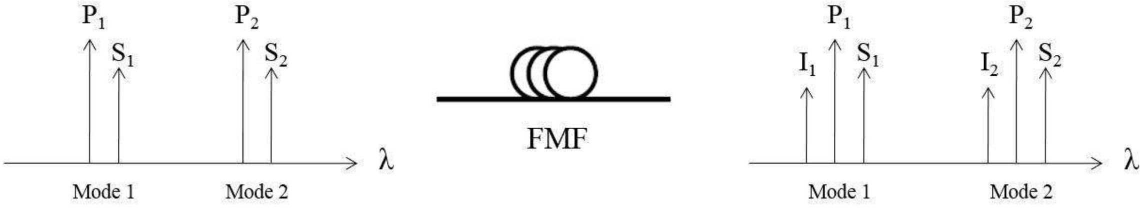

Fig. 1. Two-mode intramodal FWM

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OD6

Effect of small organic molecules on the adsorption and transport of radioactive cesium (^{137}Cs) in clay materials: From Molecular Modeling to Environmental Fate!

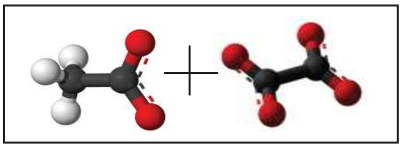
D.BANERJEE [1a], **A.KALINICHEV [1]**

[1]Laboratoire Subatech – (UMR 6457) IMT Atlantique, 4 rue Alfred Kastler, 44307 Nantes, France
[1a] banerjee@subatech.in2p3.fr

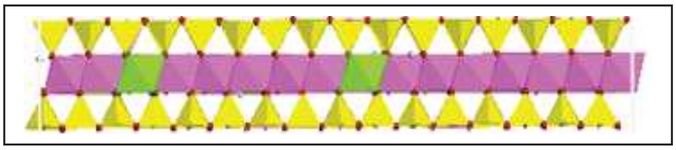
Safe and sustainable nuclear waste disposal poses major scientific challenges to the efforts to minimize the environmental footprint of nuclear energy for extremely long periods[1,2]. It has become an international consensus that geological disposal is the most appropriate way for the confinement and disposal of long lived high level nuclear waste.

Cesium-137 (^{137}Cs), an important fission product from the irradiation of uranium based fuels and it has been released in the past to soils and waters as a result of nuclear accidents or weapon testing. Radio-cesium always exists as the monovalent cation Cs^+, which has very high solubility and mobility, thus being a very relevant element from environmental point of view. Cesium migration is mostly controlled by sorption onto mineral surfaces; it is mainly adsorbed onto clays by ionic exchange[3]. Many solids have been under study for Cs retention[4] but the barriers comprised of clay materials are reported to be the most effective for its retardation. The Callovo-Oxfordian[5] clay rock formation (Meuse/Haute-Marne, France) commonly known as CO_x is the potential host rock for long term nuclear waste repository in France. The clayey component of CO_x consists mainly of illite, smectite and interstratified illite/smectite (I/S) clay minerals. It constitutes a natural external barrier for limiting these hazardous radionuclides by its CEC (cation exchange capacity) to uptake these contaminants by adsorbing them thereby restricting their transfer towards biosphere[6].

On the contrary, organic molecules that are released from nuclear waste packaging containers along with the subsequent degradation products, severely challenge our principal host rock's capacity by altering radionuclides uptake, transport in geological barrier etc. These organic complexing species are therefore known to affect radionuclide mobility in the environment.[7,8,9]



Acetate and Oxalate



2:1 clay ~ Sodium Montmorillonite representing as CO_x

In our work, we propose to perform atomistic computer simulations of a simplified but realistic model ternary system [radionuclide (RN), organic molecule (OM), COx (sedimentary clay rich host rock)] and quantitatively analyze these effects in order to increase the fundamental understanding of the various physical and chemical mechanisms controlling the interactions between them.

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Acknowledgments

Computational resources :

[1] *CCIPL- faculté des sciences de l'Université de Nantes*
[2] *Le supercalculateur Occigen du CINES*

Flash Communications

INVESTIGATION OF OXYGEN REDUCTION AT ZNO FILMS PREPARED BY RF-SPUTTERING

J. Soares Costa [a,b]*, M. Prestat [a], B. Lescop [b], S. Rioual [b], B. Tribollet [c], L. Holzer [d], D. Thierry [a]

[a] *French Corrosion Institute, 220 rue Pierre Rivoalon, 29200 Brest, France.*
[b] *Lab-STICC, UMR 6285, CNRS, UBO, 6 Avenue Le Gorgeu, 29285 Brest, France.*
[c] *Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE, 75005 Paris, France.*
[d] *Institute of Computational Physics, Zurich University of Applied Sciences, Wildbachstrasse 21, 8400 Winterthur, Switzerland.*

** corresponding author e-mail: josiane.costa@institut-corrosion.fr*

Corrosion is a local electrochemical process involving an oxidation reaction (e.g. the dissolution of a metal) that is balanced by a reduction reaction. The oxygen reduction reaction (ORR) is one of the major cathodic reactions in corrosion and more generally in electrochemistry. Oxygen can be reduced directly into hydroxyl ions or indirectly with hydrogen peroxide as intermediate species. In this Ph.D. thesis, ORR has been investigated on zinc oxide that is one the most common degraded forms of zinc, a metal of major societal and industrial interest.

Model electrodes (textured ZnO thin films prepared with ZnO target and non-textured ZnO thin films with randomly-oriented grains obtained with Zn target) have been deposited on copper substrates using RF-magnetron sputtering technique and characterized by XRD, XPS, AFM, SEM, FIB-SEM and STEM. The oxygen reduction reaction (ORR) has been investigated in KCl + KOH electrolyte (pH = 10) using rotating ring-disk electrode, a technique that allows for the electrochemical detection of hydrogen peroxyde.

During the measurement of DC polarization curves, potential-dependent rupturing of the films was observed on the layers, making the electrochemical analysis arduous. Yet it was possible to show that the direct reduction of oxygen prevailed with a non-negligible contribution of indirect reduction. Also, AC electrochemical impedance spectroscopy (EIS) was performed to characterize electrical and electrochemical properties of the textured films. EIS proved to be a powerful tool to evidence distribution of resistivity within the film and to detect more finely at which potential the rupture of the film initiates.

Research is ongoing on ZnO thin films with no preferred orientation. These layers exhibit a significantly improved mechanical stability and higher ORR activity compared to textured films. Results on the synthesis, the characterization, the mechanical stability and the oxygen reduction mechanisms will be presented for both types of films

F01

COMPARISON OF PHYSICAL PROPERTIES OF P3HT AND PBDBT-T POLYMER THIN FILMS USED IN SOLAR CELLS

L. HROSTEA[1,2,3*], **M. GIRTAN**[3], **L. LEONTIE**[1,2]

1Faculty of Physics, Alexandru Ioan Cuza University of Iasi, 11 Bd. Carol I, 700506, Iasi, Romania
2Integrated Center for Studies in Environmental Science for North-East Region (CERNESIM), Alexandru Ioan Cuza University of Iasi, 11 Bd. Carol I, 700506 Iasi, Romania
3Photonics Laboratory, (LPhiA) E.A. 4464, SFR Matrix, Angers University,Faculty of Sciences, 2 Bd Lavoisier, 49000 Angers, France
**e-mail: laura.hrostea@etud.univ-angers.fr*

This paper is based on the study of conductive polymers with photovoltaic applications: poly(3-hexylthiophene) (P3HT) and poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)- benzo[1,2-b:4,5-b'] dithiophene))- alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2ethylhexyl) benzo[1',2'-c:4',5'-c'] dithiophene-4,8dione))] (PBDBT). The polymers were deposited by spin coating on glass substrates and on ITO substrates (substrates coated with a conductive transparent oxide, indium-doped tin oxide), thus obtaining thin films with thicknesses ranging from 80 to 100 nm. These films have undergone several types of characterization. From an optical point of view, they were characterized using spectrophotometry and ellipsometry, resulting the refractive index, the extinction coefficient, the transmittance, etc. From a morphological point of view, the layers were investigated using atomic force microscopy, thus describing the roughness of the layers. The amorphous character of the layers was emphasized using X-ray diffraction, from a structural point of view. The electric resistivity of these layers was also revealed.

By comparing the results, there is an opportunity to improve the properties of these two polymers in order to increase the efficiency of solar cells, in whose structures they can be involved.

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F02

Adsorption of Quinolone Antibiotics to Goethite under Seawater-like Conditions: Application of a Surface Complexation Model

W.Cheng[1], **E.Kalahroodi** [2], **R.Marsac** [2], **K.Hanna** [*1]

[1]Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France
[2]Univ Rennes, CNRS, Géosciences Rennes - UMR 6118, F-35000 Rennes, France

*e-mail: khalil.hanna@ensc-rennes.fr (K. Hanna)

The prediction of quinolone antibiotics mobility under seawater-like conditions has been rarely studied, since accurate description of such multicomponent system is quite challenging. In our previous paper, the adsorption of a widely used quinolone antibiotic in aquaculture, Oxolinic acid (OA), to a synthetic goethite (α-FeOOH) was examined and modeled across a wide range of salinity (10−1000 mM NaCl) including seawater-like one[1]. However, cations and anions existing in seawater environments naturally or due to anthropogenic activities, could affect the mobility of OA in marine ecosystems. In this study, the adsorption of OA to goethite was examined in presence of major (e.g. Mg^{2+}, SO_4^{2-}) and trace (e.g. Cu^{2+}) ions naturally occurring in seawater. The OA adsorption can be successfully predicted using a CD-MUSIC version of the TPM over a large range of environmentally relevant conditions (Figure 1). This modeling approach allowed a quantification of the competitive and synergetic effects of different ions naturally present in seawater. The effect of SO_4^{2-} on OA-goethite binding at seawater pH (i.e. 8.2) was almost negligible, and other less abundant ions such as F^-, Br^-, BO_3^{2-} and Ca^{2+} did not exhibit a significant impact. In contrast, Mg^{2+} was found to strongly reduce OA binding via the formation of aqueous complex, while Cu^{2+} strongly increased OA sorption by forming a ternary metal-ligand surface complex. Finally, the mobility of OA in column dynamic tests can be well predicted through coupling aqueous transport and batch sorption parameters obtained in synthetic seawater. These results may have strong implications for assessment and prediction of the fate of quinolones in sediment/seawater interface systems.

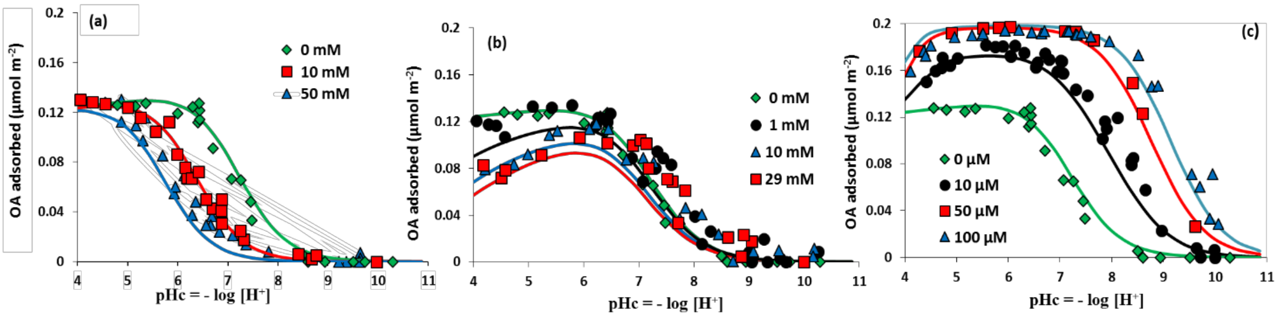

Figure 1. OA (10 μM) adsoption to goethite (50 m^2 L^{-1}) in 480 mM NaCl versus pHc at different (a) $MgCl_2$ (b) Na_2SO_4 (c) $CuCl_2$ concentrations after 24h reaction time. Lines are modeling results

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Acknowledgments

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Room-temperature plasma assisted reduction of graphene oxide films : synthesis and analysis

S. KRIDI[1], **D. DEBARNOT***[2], **F. PONCIN-EPAILLARD***[3], **N. HADDAOUI***[4]

[1,2,3] IMMM, UMR CNRS 6283 Le Mans Université, avenue O. Messiaen 72000 Le Mans, France
[4] Ferhat ABBAS University of Setif, Algeria
**e-mail: Samir.Kridi.Etu@univ-lemans.fr*

The conversion of graphene oxide (GO) to reduced graphene oxide (rGO) is a promising route to obtain graphene at low cost for various applications in nano-electronics, sensors, supercapacitors and photovoltaic devices [1-3]. In this work, we report an environmental friendly and fast approach for the production of rGO films using H_2 radiofrequency plasma at room temperature. The hydrogen plasma contains radicals and atoms which give dissociation energies for the oxygen functional groups, leading to the reduction of the GO films [1]. The graphene oxide used is synthesized from graphite via a chemical oxidation process. A freeze drying technique is employed to produce GO foams which are subsequently used to prepare stable aqueous dispersions. These are spin-coated on silicon substrates to form GO thin films. The reduction is carried out in a cold plasma reactor. Changes in sample morphology, atom composition and structural properties are studied by Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman analysis as a function of H_2 flow, treatment time and discharge power. The removal of oxygen functional groups while restoring C=C bonds is observed by XPS and Raman. The present work suggests that H_2 plasma provides a reliable approach for GO reduction and the resulting materials will be tested as electrode materials of supercapacitor.

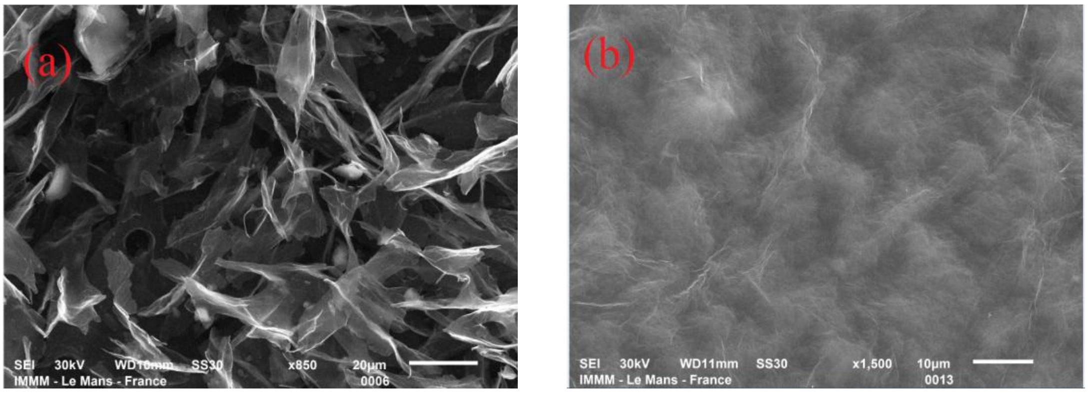

Figure 1: (a) Graphene oxide foam. (b) Graphene oxide film

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Electrochemistry- electrospray mass spectrometry coupling for the prediction of environmental and in vivo degradation of pesticides carbendazim and diuron

R. C. T. Temgoua[1,2], D. Alvarez-Dorta[1], C. Thobie-Gautier[1], I. K. Tonlé[2] & M. Boujtita*[1]

[1]Université de Nantes, CNRS, Chimie Et Interdisciplinarité : Analyse, Synthèse et Modélisation (CEISAM), UMR 6230, 2 Rue de la Houssinière, BP 92208, Nantes, France
[2]University of Dschang, Electrochemistry and Chemistry of Materials, Faculty of Science P.O Box 67, Dschang, Cameroon
**e-mail : mohammed.boujtita@univ-nantes.fr*

The prediction of environmental and in vivo degradations of xenobiotics (chemical molecules polluting and sometimes toxic inside an organism) is a theme in full emergence which is one of the major societal challenges currently at the interface of environmental and health issues. A xenobiotic (pesticides, drugs…) is characterized by various pharmacokinetic properties that define parameters such as its adsorption (wanted or not) within a living organism, its distribution, its metabolism and its excretion (ADME). The knowledge of the metabolic pathways and biotransformation of xenobiotics (pesticides in our case) is therefore essential for the elucidation of the pathways of degradation of potentially toxic substances [1,2].

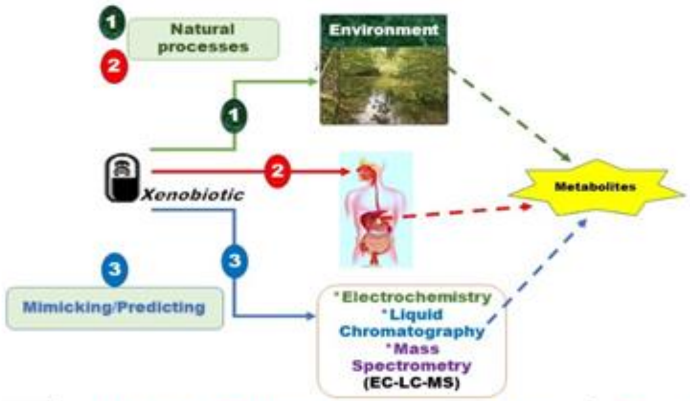
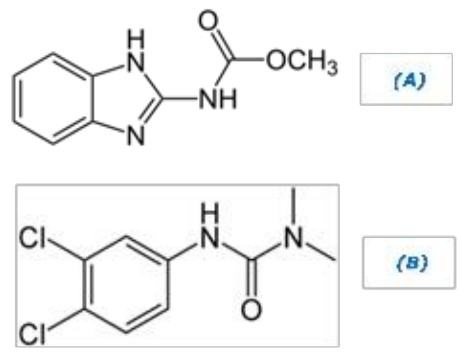


Figure 1: Metabolic pathways of a xenobiotic



Scheme 1: Structures of carbendazim (A) and diuron (B)

This work aims to highlight the exploitation of analytical and electroanalytical techniques, which combined, allow the elucidation of redox mechanisms of molecules of agrochemical interest. Through the electrochemical generation ("on-line" and "off-line") of oxidation products of different molecules, followed by their characterization and identification by mass spectrometry, we provide an answer to certain challenges posed. Oxidative phase I metabolite production was achieved using an electrochemical flow-through cell equipped with a boron-doped diamond (BDD) and glassy carbon (GC) electrodes. Known phase I metabolites of carbendazim (CBZ) and diuron (DIU) were successfully simulated by EC-LC-MS [3]. Additionally, conjugation reactions with glutathione were investigated by trapping the oxidized species before entering to mass spectrometry.

Our work consists of demonstrating, through the study of two model systems (CBZ and DIU), the utility and complementarity of hybrid electroanalytical techniques in the resolution of relatively complex oxidative mechanisms of agrochemicals that may be involved at the physiological level or in the environment.

Key words: Xenobiotic, pesticide, EC-MS, EC-LC-MS, Prediction, metabolism, in vivo

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LOCAL BINARY PATTERN BASED-METHOD FOR MULTISPECTRAL IMAGES CLASSIFICATION: APPLICATION TO MALARIA DIAGNOSIS

Yao Taky Alvarez Kossonou[1, 2], Alain Clément[2], Bouchta Sahraoui[3], Jérémie Zoueu[1]

[1] Institut National Polytechnique - Felix Houphouët Boigny-Laboratoire d'Instrumentation, Image et Spectroscopie (L2IS), Ecole Doctorale Polytechnique, BP 1093 Yamoussoukro, Côte d'Ivoire ; jeremie.zoueu@inphb.edu.ci

[2] Université d'Angers-Laboratoire Angevin de Recherche en Ingénierie des Systèmes (LARIS), UPRES EA 7315, Institut Universitaire de Technologie, BP 42018,49016 Angers Cedex, France ; alain.clement@univ-angers.fr

[3] Université d'Angers-Institut des Sciences et Technologies Moléculaires d'Angers (MOLTECH ANJOU), EA 4464 Angers, France; bouchta.sahraoui@univ-angers.fr

Abstract: Local Binary Patterns (LBP) [1] have been highly used in texture Classification for its robustness and its simple computation. Nevertheless, most of LBP methods are designed to deal with gray level images [2, 3, 4]. But some research have been done to extend LBP operator to color images. Because no natural orders exist for vectors, color order has been used to compare vectors [5]. The problem with color based-methods is their limitation to multispectral images analysis because color space only takes into account wavelengths in visible field $(400\ nm\ to\ 700\ nm)$. Another approach has been to compute LBP on each image component. Then histograms from each component after applying LBP operator are concatenated and used as texture feature. Known as marginal approach, this technique is easy to implement with disadvantage to not consider correlation existing between spectral components [6]. The pioneer LBP method for analyzing multispectral images has been designed in [7]. Termed Opponent Color Local Binary Patterns (OCLBP), it analyses multispectral image per pair of image component. The main disadvantage of this operator is its feature dimensionality. Also computing LBP on two image component at the same time, this operator doesn't consider full correlation between image components. Finally, experimentations done on OCLBP operator have provided results very close to the LBP implemented in marginal way. To better address above disadvantages, we propose a simple way to analyze multispectral images using LBP's principle. Two very simple methods have been proposed to extend LBP operators designed for gray level images to multispectral images. An evaluation of our proposals on color Outex, Vistex and Brodatz databases reveals very promising results. It showed to be robust in texture classification of images with rotation, blurring and illumination variation. The best classification scores are 99.479% for images subject to rotation, 100.00% for images with blur and 99.306% for images with illumination variation. Also, we applied our strategy on malaria samples for malaria diagnosis purpose. Using LBP based on non-absolute distance, we have been able to diagnose malaria infection.

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SCANNING X-RAY DIFFRACTION ON GAP/SI FOR III-V MONOLITHIC INTEGRATION ON SILICON

A. Zhou,[1] Y. Ping Wang,[1] A. Létoublon,[1] C. Cornet,[1] Y. Léger,[1] L. Pédesseau,[1] O. Durand,[1*] V. Favre-Nicolin,[2] G. Chahine,[2] T. U. Schulli,[2] J. Eymery,[3] M. Bahri,[4] L. Largeau,[4] G. Patriarche.[4]
[1] Univ Rennes, INSA Rennes, Institut FOTON - UMR 6082, Rennes 35000, France,
[2] ESRF, Grenoble 38000, France,
[3] Univ. Grenoble Alpes, CEA, INAC, Grenoble 38054, France,
[4] Univ Paris Sud, CNRS, C2N – UMR 9001, Palaiseau 91120, France.
**e-mail: olivier.durand@insa-rennes.fr*

The monolithic integration of III-V semiconductors on silicon is considered as a cornerstone for the coherent integration of photonics into the mature silicon technology. To this end, the epitaxial growth of quasi-lattice matched GaP on silicon (misfit of 0.37% at room temperature) has been developed to be used as an efficient platform for the subsequent integration of low-defect or defect-free III-V based heterostructures. Many strategies have been developed to suppress, reduce or filter the structural defects known to appear in such a system such as dislocations (lattice-mismatch defects), micro-twins (MTs), [1-3] or antiphase domains (APDs) [4-5] (polar on non-polar crystal growth) and which are detrimental for the applications. A remained challenge is the distribution of the misfit dislocations and their influence on the structural quality of a GaP/Si pseudo-substrate.
In this study, a nano-beam X-ray diffraction method called quicK continuous Mapping (K-Map), developed by Chahine and his colleagues at the European Synchrotron Radiation Facility (ESRF), [7] is applied to analyze our thin GaP/Si sample. 2D real space mappings of the local tilt, in-plane strain and FWHM of the scattering spot distributions are measured. Cross-hatch like patterns are observed in both the local tilt mappings and the in-plane strain mappings. The origin of the in-plane local strain variation is proposed to be a result of misfit dislocations. At last, the relationship between the in-plane strain and the free surface roughness is also discussed using a statistical method.

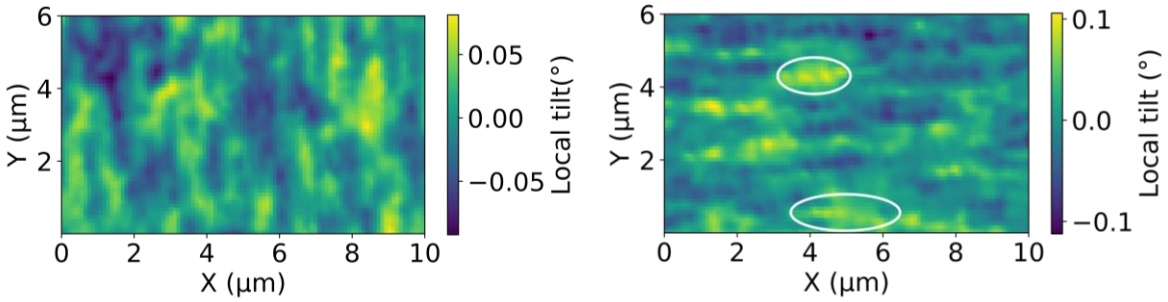

Figure1. Left: Local tilt mapping towards the [-1-10] direction using the (004) Bragg diffraction. Right: Local tilt mapping towards the [1-10] using the (004) Bragg diffraction

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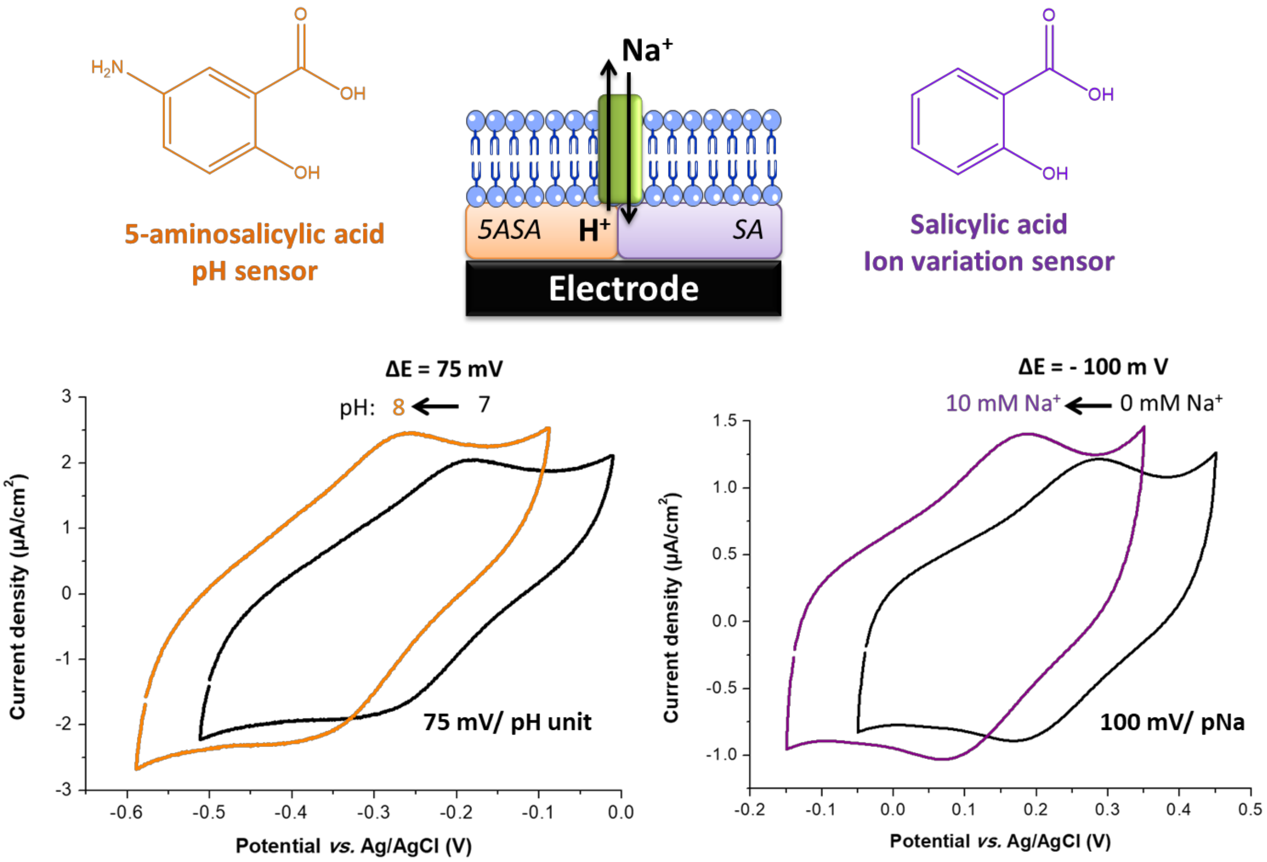
F07

FROM SALICYLIC ACIDS TO REDOX POLYMERS ENABLE TO DETECT CHANNELS ACTIVITY IN SUPPORTED LIPID DEPOSITS

T. Flinois, **E. Lebègue**, **F. Barrière**

Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR 6226, Rennes, France
e-mail : thomas.flinois@univ-rennes1.fr

Channelopathies are diseases resulting from impaired channel function; mutations in over 60 ion-channel genes are now known to cause human disease [1]. In order to detect the activities of channels onto lipid deposits (mimic of living cells membrane), we modified electrodes with two redox active polymers. One polymer from 5-aminosalicylic acid is sensitive to pH variation and another polymer from salicylic acid is sensitive to monovalent ion concentration (sodium, potassium, chloride, *etc*.). As proof of concepts, the activity of monensin an ionophores sodium/proton antiporter [2], was studied. The ionics and protons changes induced by monensin immobilized in supported lipids deposits onto the modified electrodes can be detected. These modified electrodes can also be used to study other biological transporter protein like the sodium-proton antiporter NhaA [3].



Scheme of the modified electrode with a pH-sensitive polymer from 5-aminosalicylic acid (5ASA) and a monovalent ions sensitive polymer from salicylic acid (SA). This modified electrode is used to detect the antiporter activity of monensin (in green) in supported lipid (in blue) deposit.

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Speckle imaging for monitoring the growth kinetics of Bacillus thuringiensis

H. Loutfi[1, 2,*] F. Pellen[2,] B. Le Jeune[2], R. Lteif[3], M. Kallassy[4], G. Le Brun[2], M. Abboud[1]
[1] Physics Department, UR TVA, Faculty of Science, Saint Joseph University, Beirut, Lebanon
2 Laboratoire OPTIMAG, IBSAM, Université de Bretagne Occidentale, Brest, France
3 Chemistry Department, UR TVA, Faculty of Science, Saint Joseph University, Lebanon
4 Faculty of Science, Biotechnology Laboratory, UR EGP, Saint Joseph University, Beirut, Lebanon
**e-mail: hadi.loutfi@net.usj.edu.lb, hadi.loutfi@univ-brest.fr*

Awareness concerning the usage of chemical insecticides is nowadays frequently highlighted: their negative impact on human health and environment urges scientists to find new alternatives. Among microorganisms that can be used as biopesticide, *Bacillus thuringiensis* (Bt) a Gram-positive, spore forming bacterium, is used worldwide [1]. During sporulation, bacteria synthesize spores and protein crystals. In general, biochemical methods are used to analyze the amount of parasporal crystal protein. However, these techniques have the disadvantage of being expensive and time consuming. In our work, we aim to show that laser speckle imaging can be used as an alternative low cost and reliable method to characterize the kinetic growth of Bt. Speckle is a non-destructive optical technique based on the analysis of variations of laser light scattered from diffusing samples [2]. In recent studies authors showed that speckle method can be used to distinguish crystals diameters and concentrations [3]. We present results related to the monitoring of Bt growth kinetics in a variety of culture media using dynamic polarized speckle. A linearly polarized 15 mW He-Ne laser illuminates the cellular culture and a CMOS camera collects the scattered light with a framerate of 1950 fps. Parameters such as speckle grain size and spatial contrast are determined in order to characterize the culture medium and to monitor in real time the fermentation process. Bt cells are particles with typical dimensions ranging between 3 and 5 µm that act like large scatterers with respect to the optical wavelength 0.6328 µm. In a scattering point of view, a Mie regime is manifested thus, an increase in the concentration of large scatterers in the culture medium, leads to larger D_e which will result in a decrease of the speckle grain size as shown in figure 1. In conclusion, speckle imaging analysis can be a reliable technique to follow the kinetic growth of the Bt cells [4].

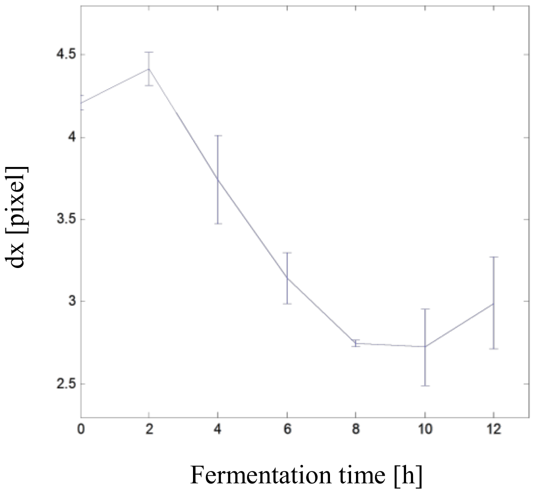

Figure 1- Variation of the speckle grain size as a function of the fermentation time. Error bars correspond to the standard deviation

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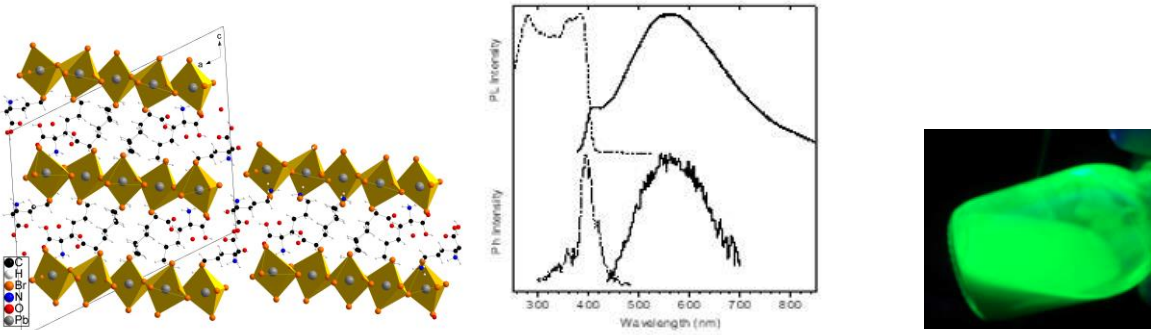
F09

HIGHLY EFFICIENT LUMINESCENCE OF HYBRID PEROVSKITES

M.BEN HAJ SALAH, [1] **N.MERCIER,** [1] **M. ALLAIN**[1] **and Chiara BOTTA** [2]

[1]*MOLTECH-Anjou, UMR-CNRS 6200, University of Angers, Angers, France*
[2]*ISMAC, CNR, University of Milano, Milano, Italy*
maroua.benhajsalah@etud.univ-angers.fr, http://moltech-anjou.univ-angers.fr/

Organic-inorganic perovskite hybrids are attracting increasing attention among scientists because the molecular hybridization offers the potential of combining the best parts of characteristic properties of the two chemical entities as well as generating new properties arising from the molecular interactions between the two building block. The rapid progress in material synthesis and device fabrication has promoted the development of optoelectronic applications including solar cells, transistors and photodetectors[1]. Moreover, (A)PbX_3 HPs have received great attention recently due to their potential application in the fabrication of very efficient light emission devices (PeLEDs for Perovskite LEDs), particularly when HPs are nanocrystals (NCs). Depending on the halide composition (X= I, Br, Cl or mixed Cl/Br, Br/I), the emission can be tuned in the all visible range.[2] *In this communication*, we report the results of our effort to prepare new materials for PeLEDS applications : **1**- a series of four hybrids materials based on 1D perovskite networks $Pb_nBr_{(4n+2)}$with n= 2, 3, 4, 5 [3](Fig. 1a). Here, the hybrid perovskite crisytallized powders display a bright orange broad-band emission (Fig 1b) with efficiencies up to 28% promoted by energy transfer processes from the inorganic to the organic moieties and display room temperature phosphorescence in the ms range [4]; **2**- Highly luminescent properties of nanocrystals of the lead and bromide deficient $(CH_3NH_3)PbBr_3$ compound, $(MA,HEA)_{1+x}[Pb_{1-x}Br_{3-x}]$ (MA^+ methylammonium, HEA^+ hydroxyethylammonium) for PeLEDS applications (Fig. 1c). These compounds are bromide derivatives of a new family of hybrid perovskite, dubbed d-HPs, that has been recently discovered in our group for PSCs applications.[5]



-a- -b- -c-

Fig. 1 a) Crystal structure of the 1D Pb_5Br_{22} perovskite network (n= 5) based compound (*DL*-$H_2Lys)_6$ $[Pb_5Br_{22}].4H_2O$; b) PLE and PL spectrum of (*DL*-$H_2Lys)_6[Pb_5Br_{22}].4H_2O$ c) Photoluminescence of NCs of $(MA,HEA)_{1+x}[Pb_{1-x}Br_{3-x}]$ upon UV irradiation.

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Poster Communications

ALDIMASSI Abdel Majid Static and dynamic properties of obliquely deposited FeCoB thin film.	**A1**
ANANTHU Sebastian MULTI-STOKES BRILLOUIN LASER.	**A2**
BOUNOR Botayna Hierarchical electrode for high areal energy on chip micro-supercapacitors.	**A3**
CHLAK Noura Development of nanostructured electrochemical microsensors for the detection of organic pesticides residues.	**A4**
COUPEAU Marina Elaboration and study of glycosylated fluorescent organic nanoparticles toward bright labelling of bacteria.	**A5**
DELVERT Alexandre Vidange d'une bulle interfaciale.	**A6**
DOUMOUYA Vassidiki Ferrites electromagnetic agility characterization technique: application to tunable antennas.	**A7**
EL FAKIR Chaimae Plant stress monitoring with active hyperspectral imaging in mid-far infrared.	**A8**
FISHER Jérôme Asymmetric Oxygenation by regulated production of singlet oxygen.	**A9**
FLORES GONZALEZ Jessica Isotopes to drive Lanthanide Single-Molecule Magnets.	**A10**
GIMENO Lea Could we promote Reductive Quenching with copper (I) diimine complexes thanks to a new chemical design of phenanthrolines?	**A11**
GIOVAGNOLI Debora 3 gamma Imaging Reconstruction for XEMIS2 Camera.	**A12**
GRENIER Laura Enable New Channels for CyTOF using Tetraazamacrocyclic-based Chelates.	**A13**
GUILLEMIN Thibaud All-solid 3D micro-supercapacitors based on MnO2 and ionogel.	**A14**
HACHEM Hadi Single Component Conductors Based on Ni(R-thiazdt(s))2 Complexes.	**A15**
HALZOUN Nadia Peptide self-assembly polymorphism and pathways	**A16**
HOBBALLAH Ahmad Synthesis and electrochemical study of mixedvalence TRIIORN clusters derived from dinuclear models of the active site of hydrogenases [Fe-Fe].	**A17**
JAHJAH Walaa Influence of mesoporous or parasitic BiFeO3 structural state on the magnetization reversal in multiferroic BiFeO3 / Ni81Fe19 polycrystalline bilayers.	**A18**
JANI Aicha Toluene/butanol binary solvents confined in periodic organosilicates: New insight from neutron diffraction studies.	**A19**

JEBALI Nessim Chalcogenide photonic integrated platform for near- and mid-infrared applications.	**A20**
KARUVATH Amith Tunable coherent sources for sensors or telecom applications.	**A21**
KHALIL Montassar Synthesis of amphiphilic compounds by click chemistry.	**A22**
LELONG Evan Synthesis strategy for cyclam-derivatives cobalt-complexes able to modulate amyloid-β aggregation.	**A23**
LEVCHUK Artem Probing the ultrafast response of Bi2Te3 induced by Near-IR and THz femtosecond pulses.	**A24**
LOUVET Geoffrey Er3+-doped Ga-Ge-Sb-S glass thin films by PVD deposition.	**A25**
MANAGUTTI Praveen A layered double perovskite: In situ exsolution and integration of transition metal nanoparticles as a catalyst for efficient SOFC anode.	**A26**
MARLIN Axia C-functionalized 1,4,7-Triazacyclononane (TACN) synthesis for bifunctional chelators for positron emission tomography imaging.	**A27**
MURAVYEVA Viktoria Heterometallic clusters [Re6-xMoxSe8 (CN)6]n- (x = 1–3): preparation and properties of the compounds with different Re/Mo ratio.	**A28**
PARKER Norbert Circulateurs en bande Ku en technologie collective multicouche.	**A29**
PHILIPPE Clotilde Synthesis of novel thiorescent tetracyanobutadienes towards new AIE fluorophores.	**A30**
POPCZYK Anna Magdalena Influence of donor and acceptor substituents on photoinduced optical birefringence in novel thiophene derivatives.	**A31**
PREVOSKA Tereza Isolation and characterisation of hydroxyproline-rich glycoproteins from green macroalga Ulva lactuca.	**A32**
RAIMONDEAU Kevin Performance improvements of a nematic liquid crystal dichroic dye mixture by addition of a chiral dopant.	**A33**
REGNACQ Matthieu Etudes par électrochimie et spectrométrie de masse d'un catalyseur [Cu(bpy)]+/TEMPO pour l'oxydation de l'alcool benzylique en benzaldéhyde.	**A34**
RUEL Louis Induced transparency by coupling of WGM active resonators.	**A35**
SALMA Alaa Platform molecules: production and applications, case study succinic acid.	**A36**
SARR Serigne Etude Théorique de liaison halogène impliquant l’astate.	**A37**

SENGAR Atul Development of a Beam Loss Monitor and Transverse Beam Dynamics Studies at ARRONAX C70XP Cyclotron	**A38**
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Static and dynamic properties of obliquely deposited FeCoB thin film

A.M Aldimassi[1], A. Chevalier[1] , J. Ben Youssef[1] ,V. Laur[1] and B. Rouvellou[1]

[1]*Lab-STICC, UMR CNRS 6285, Université de Bretagne Occidentale, 6 avenue Le Gorgeu, CS93837, 29238 Brest Cedex 3*
`Abdel-Majid.Aldimassi@univ-brest.fr`

Microwave circuits are used in the field of telecommunications or non-contact sensors. They are a component of the transmission / reception chains (antennas, filters, impedance matching and amplification). High levels of miniaturization, efficiency and integration are therefore in great demand for passive components. The soft magnetic thin film with high value of permittivity and/or permeability has become an important study. The ferromagnetic resonance frequency *fmr* increases with the increasing of the value of the magnetic anisotropy field *hk* and the saturation magnetization according to Kittel equation [1]. Recent works are based on obtaining a high value of uniaxial anisotropy field. In order to obtain a high anisotropy field, there are several methods such as applying DC magnetron sputtering [2], exchange bias coupling [3], pre-stressed materials [4] and oblique deposition [5].
One of the best and easiest ways to tune the uniaxial anisotropy field is the oblique deposition by magnetron sputtering. FeCoB is a good candidate to achieve a high saturation magnetization [6].
High boron concentration [7] in FeCoB leads to amorphous material. The static and dynamic magnetic properties of obliquely sputtered FeCoB thin film have been investigated. Structure and morphology are analyzed using an X-ray diffraction and an atomic force microscopy respectively. The values of the anisotropy field and the saturation magnetization are given using a vibrating sample magnetometer in static measurements. In dynamic measurements the values of the resonance frequency are deduced using a permeameter. The figure below shows the comparison between the experimental (dynamic measurements) and calculated (deduced from static measurements) resonance frequencies at different oblique angle from 0° to 75°.

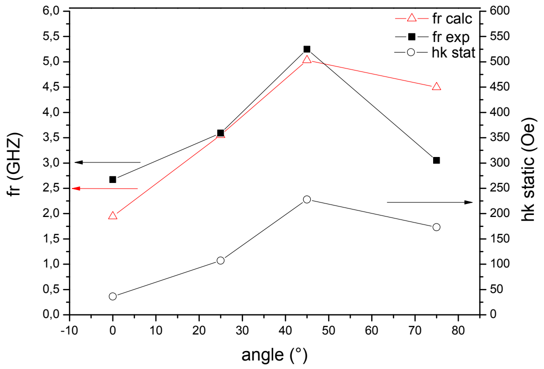

Fig.1. Dependence of the resonance frequency and the anisotropy field on incidence angle.

Calculated and experimental fmr frequencies are in good agreement; both follow the evolution of the anisotropy field as expected. This behavior will be discussed at the conference.

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MULTI-STOKES BRILLOUIN LASER

A. Sebastian, I. V. Balakireva, S. Trebaol, and P. Besnard
Univ Rennes, CNRS, Institut FOTON - UMR 6082, F-22305 Lannion, France*,*
**e-mail: ananthu.sebastian@univ-rennes1.fr*

Highly coherent lasers are needed for applications in coherent optical communications, remote sensing and microwave photonics [1]. Brillouin lasers (BL) are good candidates for such sources. It is based on Stimulated Brillouin Scattering (SBS), for which an optical wave, called the pump, is used to generate, in a material like a silica fiber, a back-scattered signal, called Stokes 1 (S1). The seeded signal or the pump, creates a Brillouin gain (shifted by 10.8 GHz from the pump wavelength, in silica and with a bandwidth of ~10 MHz), that can be used to realize a laser named Brillouin Laser (S1BL) [2]. To optimize the performances of such a Brillouin laser, both the pump and Stokes waves must be resonant within the ring cavity, which means an adjustment of the laser cavity length and/or the pump wavelength. It is well known that the S1 wave may have better coherent properties that the pump [3]. In BL, pump phase noise is transferred to S1 with significantly reduced magnitude due to the combined action of acoustic damping and cavity feedback. S1 could itself act as a pump for second wave S2 and noise reduction could be thus cascaded as proposed by Tow [3], Vahala [4]. We made a Brillouin Multi-stokes fiber laser (MSBFL) using 20 m polarization maintained fiber. This fiber ring cavity is resonantly pumped using a continuous wave laser [1]. The different output powers (S1 (blue), S2 (green), and S3 (yellow)) of this cascaded Brillouin laser are shown in figure 1 in solid lines (left axis) as function of input pump power. When the power in S1 reaches the normalized output power needed to compensate linear losses of S2, coherent emission of S2 takes place; the cascaded process is on. In that regime, the S1 circulating power is clamped. If the frequency noise reduction is well established for S1BL [3] and recently established for multi-Stokes laser [4,3,1], it is extraordinary to get a reduction for both the intensity and the phase of the generated output laser S1. We have shown that intensity noise reduction is obtained for S1, when S2 threshold is reached [5] and is due to gain saturation of S1[6].

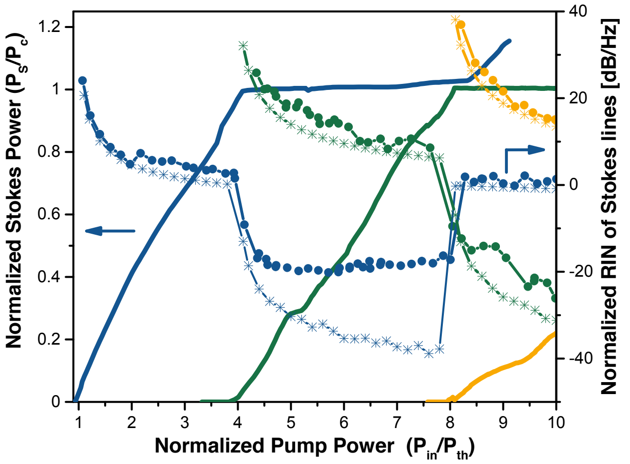

Figure 1 : laser output powers (left axis) and normalized RIN reduction (right axis) of the different Stokes waves with respect to the input pump power .

In figure 1 (right axis), noise reduction is shown through Relative intensity noise (RIN) of individual Stokes with respect to the input pump power. The RIN is normalized by the pump RIN: a zero value means that the pump and the Stoke waves have the same intensity noise (RIN). Above 4×Pth, which corresponds to the S2 lasing threshold, the S1 experiences an abrupt RIN reduction up to 20 dB compared to the input pump RIN level. This reduction originates from the clamping effect of S1 line due to the appearance of the stimulated S2 emission. Dotted lines correspond to measured RIN and starred lines to numerical simulations based on a set of coupled-mode equations.

During my Ph.D. thesis, several advances have been made:

1. New method of characterizing Brillouin gain in material by cavity-ring down spectroscopy
2. A theoretical description of noise reductions in MSBFL [6].
3. The ultimate limits of frequency noise reduction and its theoretical counterpart.
4. A perfect match of intensity noise reduction between experimental and theoretical results, showing that even a 40 dB reduction is possible,

The last achievement is the object of this presentation. This Ph.D. project gives inputs to designing optimized Brillouin fiber laser in terms of noise reduction.

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HIERARCHICAL ELECTRODE FOR HIGH AREAL ENERGY ON CHIP MICRO-SUPERCAPACITORS

B. Bounor[1,2,3,4], C. Douard[1,4], F. Favier[3,4], T. Brousse[1,4], C. Lethien[2,4]

[1]IMN JR CNRS UMR 6502, Nantes University, France
[2]IEMN CNRS UMR 8520, Lille 1 University, France
[3]ICGM CNRS UMR 5253, Montpellier II University, France
[4]RS2E FR 3459 CNRS, France

** botayna.bounor@etu.univ-nantes.fr*

With the development of various technologies including electrical micro-systems and wireless technology, the question of miniaturization of energy storage devices arises. Micro-supercapacitors[1–2] (MSCs) with high energy densities and unlimited lifetime would provide a good autonomy for connected smart objects. So, in our study, top-down and bottom-up syntheses were combined for the development of hierarchical electrodes based on 3D silicon microstructures decorated with SiO_2 nanowires (NWs). These 3D silicon scaffolds (walls, tubes) are fabricated using microfabrication techniques by combining photolithography and Deep Reactive-Ion Etching (DRIE) of a silicon wafer to further increase the surface area. SiO_2 nanowires are generally prepared by the solid-liquid-vapor method by introducing a metal catalyst. The key point of the proposed study to efficiently coat the 3D scaffold with SiO_2 nanowires deals with the deposition of conformal metal catalyst thin film on high aspect ratio microstructures. To reach this goal, platinum (Pt) thin film is deposited by Atomic Layer Deposition (ALD). This deposition method ensures the conformality of the deposit on the 3D scaffold, which allows the uniform growth of SiO_2 nanowires along the 100 µm-depth high aspect ratio structures. SiO_2 nanowires have been synthesized by Rapid Thermal Annealing[3] (RTA) of SiO_2/Pt thin films. In this study, we investigated manganese dioxide (MnO_2) as electrode material. High specific area samples were firstly coated with a 50 nm-thick Pt layer which acts as a current collector and MnO_2 seed layer. Then, MnO_2 thin film was deposited by pulsed electrodeposition in 0.1M $MnSO_4$ / 0.1M H_2SO_4 electrolyte to make a conformal deposition. First electrochemical measurements in liquid electrolyte (5M $LiNO_3$) between 0 and 1 V vs Ag/AgCl of 3D electrode based on micro-tubes show a promising capacitance of 750 $mF.cm^{-2}$ at 2 $mV.s^{-1}$ and 140 $mF.cm^{-2}$ of 3D electrode based on SiO_2 (NWs). By combining these nanostructured electrodes based on SiO_2 NWs with 3D microstructures, the surface gains will be cumulated, to reach higher surface capacitance (>2000 $mF.cm^{-2}$).

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Development of nanostructured electrochemical microsensors for the detection of organic pesticides residues

N. Chlak[1*], A. Chmayssem[2], F. Jaber[2], D. Hauchard[1]

1: Université de Rennes, Ecole Nationale Supérieure de Chimie de Rennes (ENSCR), CNRS, ISCR-UMR6226, F-3500 Rennes, France
2: Lebanese University, faculty of sciences I, Laboratory of Organic Compounds Analysis (LACO), Hadath, Beirut, Lebanon
3: CEA, Laboratory of Electronic and Information Technologies (LETI), MINATEC Campus, 38054 Grenoble, France
*noura.chlak@hotmail.com

In our project, we develop new electrochemical micro-sensors for the trace detection of targeted pesticides with nanostructured composite materials introduced into 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 micro-sensors by cyclic voltammetric techniques after an adsorption step on the composite material included in a cylindrical microcavity (Ø = 50 µm, h = 17 µm). Carbon pastes in the CME electrode are constituted by micro-sized carbon powders mixed with multiwalled carbon nanotubes and nano-copper oxide particles. Now four pesticides (isoproturon, linuron, fipronil and bentazon) have been studied.

After optimisation of experimental conditions (adsorption times, cyclic voltammetry parameters, pH), the best results are obtained with the herbicide isoproturon (ISO,) with a notable detection limit of $4x10^{-10}$ mol.L^{-1} (≈20 ng.L^{-1}) in aqueous acid medium and $4x10^{-8}$ mol.L^{-1} in electrolyte containing acetonitrile (ACN). The calibration curves were linear from 6.10^{-9} M to 10^{-6} M and it appears that, for water samples, standard addition method is recommended to a better accuracy.
Actually, we detect traces of ISO in aqueous/organic mixed solutions. We should expect the detection in vegetables samples after extraction by ACN.

Elaboration and study of glycosylated fluorescent organic nanoparticles toward bright labelling of bacteria

M. Coupeau[1*], J. Boucard[1], L. Lartigue[1], E. Ishow[1]

[1]CEISAM Laboratory, UMR CNRS 6230, University of Nantes, 44322 Nantes, France
**e-mail: marina.coupeau@univ-nantes.fr*

Fast and selective detection of pathogens represents high challenges given the considerably high proliferation rate of bacteria and their mutation potential against antibiotics. Moreover, to be fully efficient, detection needs to be selective for bacteria. In this study, we are interesting in pathogenic *Escherichia coli*, responsible for gastrointestinal and urinary tract infections. These bacteria express *fimbriae* that display strong binding to mannose. Recently, we have developed fluorescent organic nanospheres (FONs) functionalized with phosphonic acid units[1] that interact within 5 minutes with *Staphylococcus aureus*[2]. Our aim here is to extend this strategy to glycosylated FONs to label *E. coli* membrane.

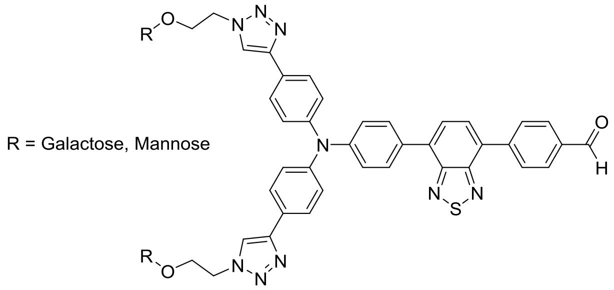

Figure 1 : Structure of the glycosylated fluorophores.

For this purpose, we have fabricated two kinds of glycosylated fluorophores which incorporate a benzothiadiazole unit, known for its high photostability and red fluorescence efficiency (Figure 1). A modular approach based on rapid and versatile Click-Chemistry allowed us to graft glycosylated moieties (galactose and mannose).

These fluorophores were self-assembled as FONs upon nanoprecipitation. Compared to free dyes in solution, they provide higher brightness and near-infrared emission (λ_{max} = 640-680 nm), which limits the autofluorescence signal in living organisms. Moreover, these ultrabright dots are nontoxic and show high potential recognition due to a high payload of glycosylic groups.

Concanavalin A, a lectin specific to mannose[3], was used as a nonpathogenic model to apprehend interactions between FONs and *fimbriae* of *E. coli*. Preliminary results involving fluorescent *ConA* show significant fluorescence resonance energy transfer (FRET) from mannose-FONs to the lectin, proving close vicinity of both partners and thus complexation of mannose-FONs by *ConA*. Comparative studies on galactose-FONs show no such FRET, evidencing high selectivity of the recognition process. This feature offers promising perspectives to use mannose-FONs as diagnostic agents to label *E. coli* cells in a rapid and specific way.

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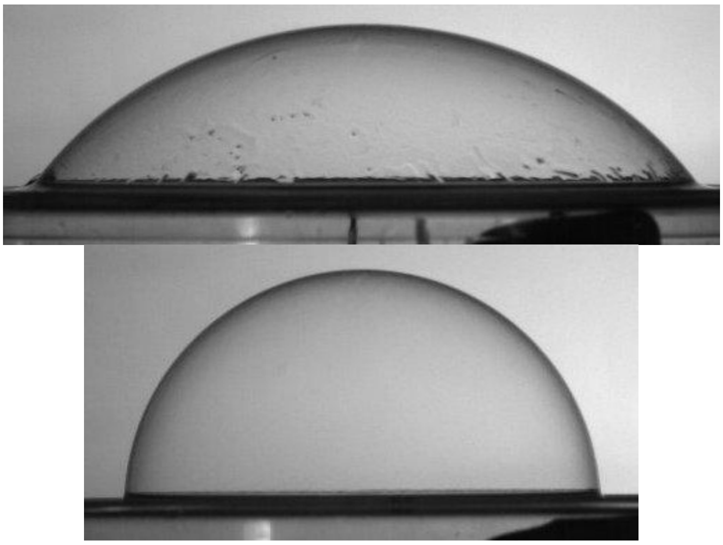
Vidange d'une bulle interfaciale

<u>A. Delvert</u> **, P. Panizza, L. Courbin**

Institut de Physique de Rennes
alexandre.delvert@univ-rennes1.fr

Nous nous sommes intéressés à la vidange d'une bulle posée sur un substrat. En effet des travaux ont été réalisés sur le drainage et l'éclatement des bulles de savons. La question se posait alors de savoir quels phénomènes apparaissaient si l'air contenue dans une bulle se vidait par un trou présent sur le substrat. Nous avons observé plusieurs dynamiques qui agissent directement sur le temps de vidange. En faisant varier la taille du rayon d'ouverture du trou on peut contrôler le régime d'écoulement d'air sortant de la bulle. On peut faire varier la viscosité de la solution qui influe sur les frottements visqueux présents au point de contact entre la bulle et le substrat. Le model proposé permet d'établir l'existence de deux comportements : l'effondrement de la bulle et le dégonflement visqueux.



Ferrites electromagnetic agility characterization technique: application to tunable antennas

V. Doumouya[1], V. Laur[1], P. Queffelec[1], J. L. Mattei[1], A. Chevalier[1]
[1]Lab-STICC, Université de Brest, CNRS, Université Bretagne Loire, Brest 29238 Cedex 3, France
vassidiki.doumouya@univ-brest.fr

This work is part of the ANR MISTRAL project. One of the objectives of this project is to design VHF-tunable miniature tunable antennas based on magneto-dielectric materials for aeronautical applications. The principle of tunability of the antenna is based on the use of dense soft toroidal ferrites whose variations in permeability induce a change in the frequency of operation of the antenna. It is thus essential to determine the evolution of the electromagnetic properties (EM) of the ferrites under the action of an external static current, and thus, to propose a method of characterization in an EM field configuration and static control corresponding to the final application. On the experimental level, EM ferrite characterization is commonly performed in the demagnetized state by using the reflection / transmission technique based on the use of a coaxial line [1].In the saturated state, the measurement of the half-height line width ΔH (or ΔHeff) can be performed in resonant cavity [2], and the extraction of anisotropic permeability in microstrip or triplate lines [3]. The soft ferrites, developed at Lab-STICC as part of the project, are toroidal in shape. The toroidal shape has many advantages for integration into an agile antenna. If the sample surrounds a strand of the antenna, it is possible to apply a current in the conductor so as to modify the properties of the ferrite. Moreover, the toroidal shape makes it possible to limit the macroscopic demagnetizing effects in the orthoradial direction, and thus, to optimize the permeability variations for a given external field. The characterization method must be adapted to the final integration of the material into the antenna. Thus, in this article, we propose to adapt an APC7 coaxial line characterization method to extract the permeability of ferrites under the action of a current (Fig. 1). The current is applied in the core of the coaxial line in the direction of propagation and creates a static orthoradial magnetic field.

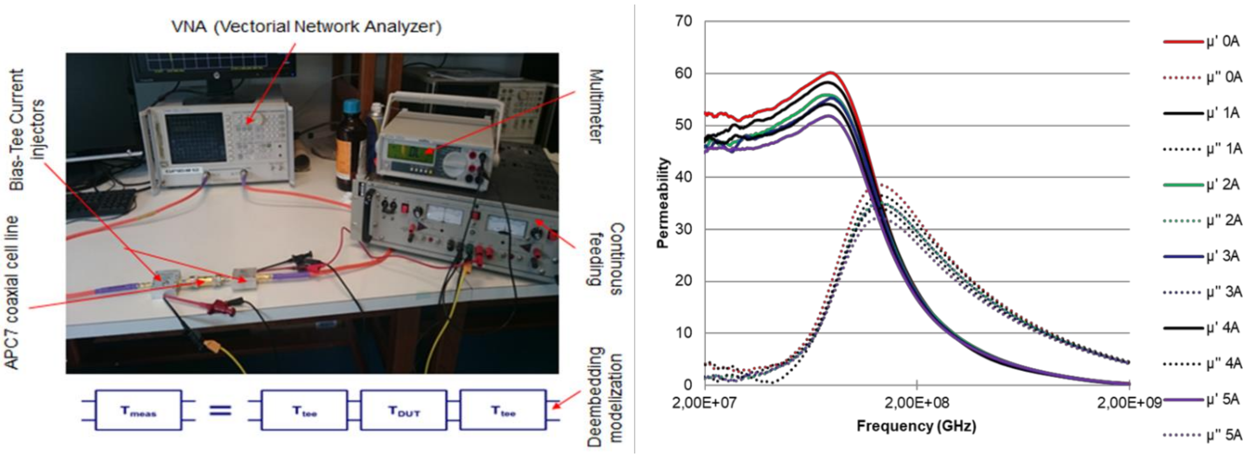


Fig. 1. Measuring bench of ferrite dynamic agility under current modeled by chain matrices and measurement results.

In order to overcome the observed variation of the dynamic response of the bias tees (used to inject a current in the coaxial line), a modeling using transmission matrix (T) of the tee-cell-tee assembly has therefore been proposed (Figure 1 at the bottom left) and implemented using MATLAB programs. Fig. 1 (right) shows the permeability spectra of a soft ferrite developed at Lab-STICC for different current values. This material has an almost constant agility of about 12% on the VHF band that can be exploited for the design of a tunable antenna. The measured spectra can therefore be integrated into an EM simulator (HFSS) in order to design an agile antenna that can be controlled with a current.

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Plant stress monitoring with active hyperspectral imaging in mid-far infrared

Chaimae El Fakir[1], **Luiz Poffo**[1], **Bastien Billiot**[2], **Pascal Besnard**[1], **Jean-Marc Goujon**[1]

[1]*Univ Rennes, CNRS, Institut FOTON - UMR 6082, F-22300 Lannion, France*

[2]*Agro Innovation International-CMI, 35400 Saint-Malo, France*

chaimae.elfakir@univ-rennes1.fr

Stress in plants cause major production and economic losses in agriculture. This stress can be generated from biotic and abiotic factors such as diseases, insects or climatic conditions. Water stress is one of the most critical abiotic stressors limiting plant development. Monitoring this stressor has been mainly detected after destructive sampling followed by biochemical and molecular determinations. Currently, spectroscopy is most widely used for identifying characteristics of leaf (such as water content, size, height and area) to assess the plant health and stress status. The effect of stress on the spectral properties in thermal band, between 3 µm and 14 µm, has been investigated in 2016 and 2017 [1,2] by using a spectrometer that needs to prepare the plant samples before measure.

Thermal imaging and the recent availability of widely tunable infrared QCL lasers (Quantum Cascade Laser) allows us to propose a multispectral (disjoint spectral bands) and a hyperspectral (continuous bands) imaging system to characterize stress in plants without preparation, *in situ*.

In order to evaluate more precisely the capacities of the proposed system, we have developed an experimental bench at laboratory, under controlled growing conditions, to determine the variations of spectral reflection and transmission of plants in different water stress conditions. Monitoring this plants by imaging techniques could help to identify changes in their characteristics in an early stage, before it can visibly be detected.

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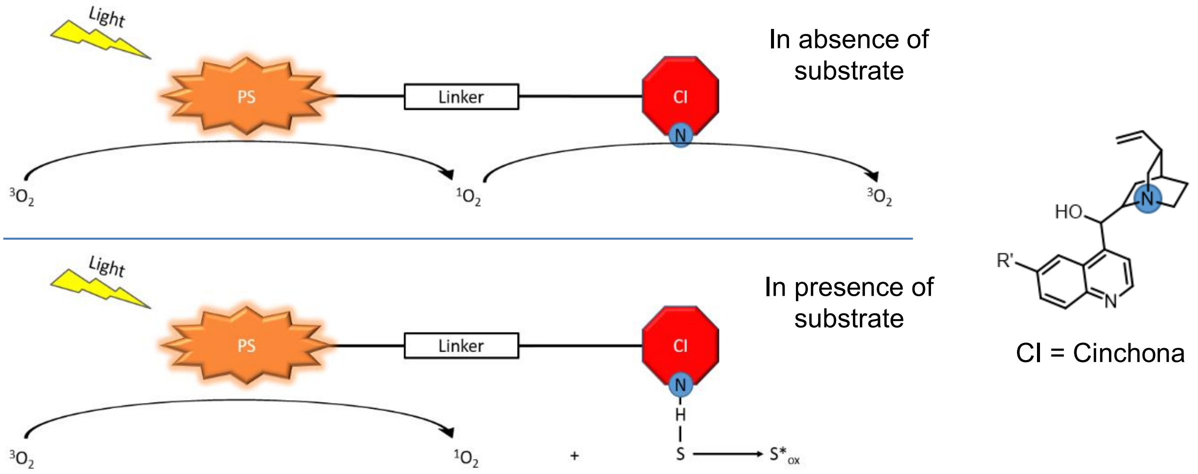
ASYMMETRIC OXYGENATION BY REGULATED PRODUCTION OF SINGLET OXYGEN

J. Fischer[1], V. Coeffard[1], P. Nun[1], H. Brault[2]

[1]Université de Nantes, CEISAM, Faculté des Sciences et Techniques, 2 rue de la Houssinière, 44322 NANTES Cedex 3, [2]Université de Nantes, Institut des Matériaux Jean Rouxel, Faculté des Sciences et Techniques, 2 rue de la Houssinière, 44322 NANTES, Cedex 3

Singlet oxygen ($^1O_2$) is an excited state of the O_2 – molecule, which has applications in biology, materials and chemistry.[1] In synthesis, singlet oxygen is often produced with photosensitizers and used in photooxygenation. These reactions offer great advantages (profusion of oxygen, atom economy, low catalytic charges needed, etc.) and researchers work on reaching the full potential of it. However, regio- and enantioselectivity is hard to master due to the very high reactivity of $^1O_2$ and asymmetric photooxygenation processes are limited and lowly efficient.

Some works have been performed on asymmetric catalytic systems where photosensitizers are directly linked to chiral inducers (sugars, proline, bisoxazolines, etc.), but only low yields and enantiomeric excess (ee), on a limited range of substrates, were obtained.[2,3,4] The poor results are due to the constant production of singlet oxygen, which can react with non-activated substrate, causing non-asymmetric photooxygenation.



Scheme 1: Regulation of $^1O_2$ production depending on the presence of substrate (PS = photosensitizer, CI = chiral inducer) and general representation of cinchona's family

Our strategy is to control the production of singlet oxygen by using a chiral inducer which could be able to deactivate $^1O_2$ in absence of substrate and to transfer chirality in presence of substrate (Scheme 1). Cinchona's family has been chosen in the role of chiral inducer, taking advantage of their ability to deactivate $^1O_2$. Indeed, these molecules have a tertiary amine, which interact with $^1O_2$ by non-destructive physical interaction when its electron lone pair is free.[5]

Photooxygenation has been first tested and optimized with separated photosensitizer and chiral inducer. Then, a synthesis of a chiral photosensitizer has been performed, to increase the influence of the chiral inducer on the system. Finally, a screening of different substrates has been led to observe the efficiency range of our asymmetric catalytic system.

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ISOTOPES TO DRIVE LANTHANIDE SINGLE-MOLECULE MAGNETS

J. Flores Gonzalez,[1] L. Ouahab,[1] F. Pointillart*[1] & O. Cador *[1]

[1] *Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1*
263 Avenue du Général Leclerc 35042 Rennes Cedex (France)
Jessica.flores-gonzales@univ-rennes1.fr

Lanthanides play an important role in the field of molecular magnetism. Complexes based on these trivalent cations possess strong magnetic anisotropy and high magnetic moment, crucial for enhancing the energy barrier and therefore displaying a slow relaxation of their magnetization and magnetic hysteresis at low temperature, which are the properties making them interesting for their use as Single-Molecule Magnets (SMMs).[1]
In the group special attention has been paid to dysprosium mononuclear-complexes that due to its high anisotropy, result in an ideal candidate to retain the magnetic information in zero field. However, several examples[2,3] show the appearance of a fast relaxation time at sufficient low temperatures in comparison with the energy barrier. This is explained by the existence of intramolecular (hyperfine) and intermolecular (dipolar) interactions that make possible other relaxation pathways. For that reason, effort has been focused in understanding the relation between the relaxation effects and the contributing interactions, by playing with pure isotopic metal centers and magnetic dilutions.[4]
Dysprosium is mainly constituted by four stable isotopes with different nuclear spin ^{161}Dy and ^{163}Dy, with I=5/2, and ^{162}Dy and ^{164}Dy, with I=0. Dy^{III}-based mononuclear complexes have been synthesized following the previous considerations: 1) isotopic enrichment in order to play with the hyperfine interactions, and 2) magnetic dilution to isolate the molecule from the neighboring complexes. A full dynamic study of the magnetic response has been carried out and the different results have been compared in order to distinguish a similar trend in the magnetic behavior. [4,5]

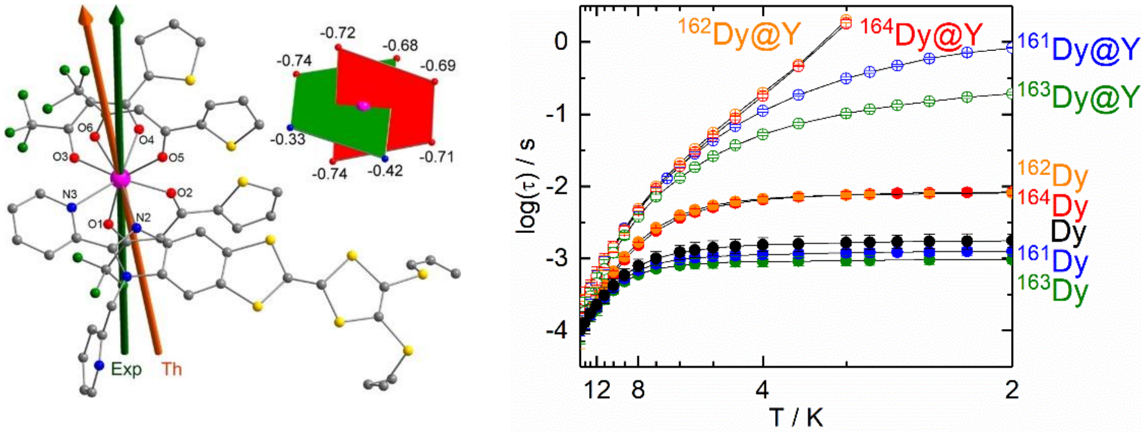

Figure 1. (On the left) X-ray structure of Dy^{III}-Complex with higher anisotropy tensor vectors; (On the right) Temperature dependence of the relaxation time (τ) at 0 Oe for both pure-isotopic (^{A}Dy) and magnetic diluted (Dy@Y) complexes.

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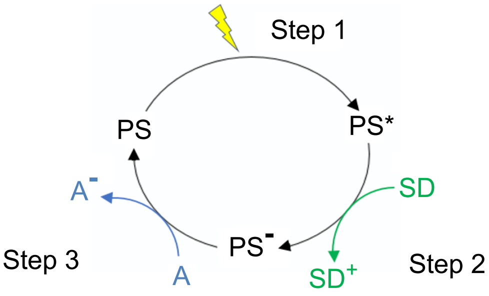
Could we promote Reductive Quenching with copper(I) diimine complexes thanks to a new chemical design of phenanthrolines?

L. Gimeno, E. Blart and Y. Pellegrin

Nantes University, 2 chemin de la houssiniere, France
Lea.gimeno@univ-nantes.fr

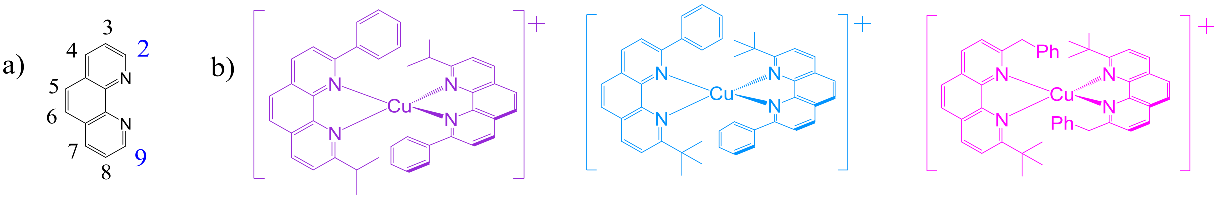
Reductive quenching is the best way to do difficult reduction with light. After excitation of a photosensitizer (PS) is promoted into it excited state (PS*) (step1 in figure 1). The key step is the transfer of one electron to PS* from a sacrificial electron donor leading to PS$^-$ (step 2). PS$^-$ is then able to reduce a substrate A if the thermodynamic potentials are adequate (step 3).
Copper (I) diimine complexes have been chosen as PS because of their very low reduction potential. For example $[Cu(dpp)_2]^+$ and $[Cu(ipp)_2]^+$ half-wave potentials are respectively -2.10 and -2.21 V vs Fc$^{+/0}$ for the couple PS/PS$^-$[1]. In this model, an issue remains: copper diimine complexes are known to be poorly oxidant in the excited state so step 2 is thermodynamically uphill.

In order to address this issue, we aimed at increasing the oxidation potential in the excited state (Eox*) by a new chemical design of phenanthrolines. Every modification of the phenanthroline will directly impact the potential Eox* of the copper complex. In that way we tried to balance steric hindrance brought by the substituents in the positions 2 and 9 of the phenanthroline (which are mandatory to promote the excited state properties of the copper complexes) and the stability issue induced by the steric strain of this same substituents. Phenanthroline was namely substitued in position 2 by a bulky aliphatic group (to promote luminescence) and position 9 by an aromatic group (to stabilize the coordination sphere by intramolecular π-stacking). Thus, we designed three new ligands $[Cu(ippp)_2]^+$, $[Cu(tbpp)_2]^+$ and $[Cu(tbbzp)_2]^+$ composed of one aromatic stabilizing group able to do π-staking with vicinal phenanthroline ligands in the copper(I) complex and one bulky ramified alkyl group. We studied the impact of the latter (using both iPr and tBu) as well as the effect of a spacer between phenanthroline and the aromatic ring (CH_2 vs. direct bonding). This presentation will focus on the synthesis, the photophysical characterizations, stability study and first tests of reductive quenching of this family of three copper(I) complexes with asymmetric phenanthrolines ligands.



PS: Photosensitizer
SD: Sacrificial donnor of electron
A: target substrate

Figure 1: Reductive quenching mechanism



$[Cu(ippp)_2]^+$ **$[Cu(tbpp)_2]^+$** **$[Cu(tbbzp)_2]^+$**

Figure 2: a) Phenanthrolines numbering b) Family of copper(I) complexes.

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3 gamma Imaging Reconstruction for XEMIS2 Camera

D. GIOVAGNOLI[1]

[1] INSERM, UMR 1101, LaTIM, IMTAtlantique, University of Western Britanny, Brest, France

Abstract – XEMIS2 (XEnon Medical Imaging System) is a Liquid Xenon Time Projection Chamber that provides a 3 dimensional image of a low radioactive source using a new imaging technique that exploits Sc-44, a 3 gamma emitter. This will allow to decrease patient dose by a factor 100. A complete Monte Carlo simulation of the detector is used to study a new reconstruction algorithm that will fully benefit of the additional information from the third gamma. The core idea is to exploit the information carried by the third gamma associating a probability density to each Line Of Response. Since this gamma is more energetic (1.157 MeV) than the two annihilation photons (511 keV), it mostly interacts in the detector through Compton scattering. The crossing point between the LOR and the Compton cone allows to locate the interaction on the LOR with an accuracy of less than 1 cm. A study of the probability density has been made in function of the angle between LOR and cone. CASToR (Customizable and Advanced Software for Tomographic Reconstruction) software was used to perform reconstruction. First preliminary experiments focused on testing the non-standard XEMIS2 geometry in CASToR with 2 gamma reconstruction using LORs with a uniform probability density.

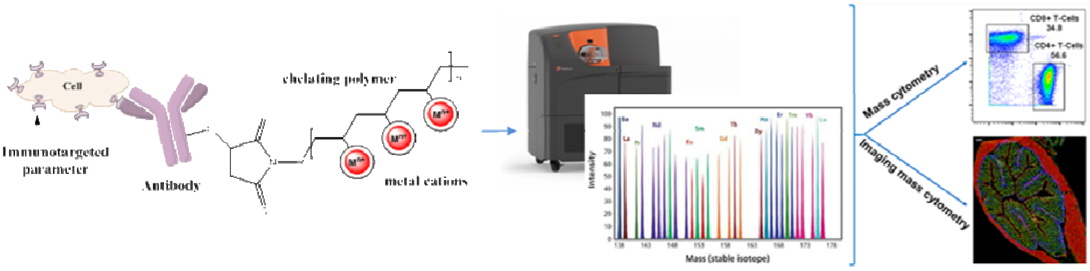
Enable New Channels For CyTOF Using Tetraazamacrocyclic-Based Chelates

L. Grenier[1]*, **M. Beyler**[1], **P. Liu**[2], **V. Baranov**[2], **R. Tripier**[1]

[1]UBO, UMR CNRS 6521 « Chimie, Electrochimie Moléculaires et Chimie Analytique », IBSAM, 6 av. Victor Le Gorgeu, 29238 Brest ; [2]Fluidigm Canada Inc., Markham, Ontario, L3R 4G5
**e-mail: laura.grenier@univ-brest.fr*

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.



[4]

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 watersoluble 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.

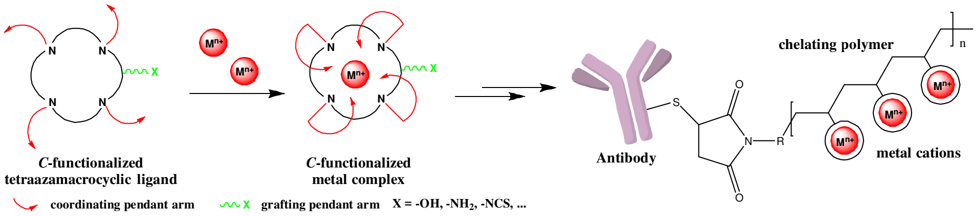


Figure 2. Tetraazamacrocyclic-based chelates

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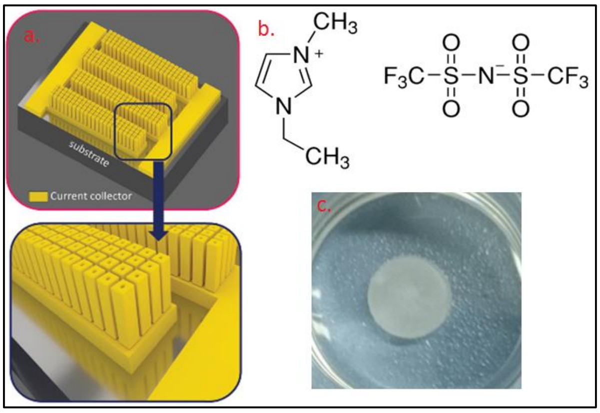
All-solid 3D micro-supercapacitors based on MnO_2 and ionogel

T. Guillemin, C. Douard, A. Marie, T. Brousse J. Le Bideau*

Institut des Matériaux Jean Rouxel (IMN), 2 Chemin de la Houssinière 44300 Nantes
**e-mail: jean.lebideau@cnrs-imn.fr*

Micro-supercapacitors are energy storage micro-devices designed to be used in portable electronics, sensors and IOT [1]. They are assessed for their high power density and long cycle life. The energy density can be improved by working on the architecture of the micro-supercapacitor and the use of pseudocapacitive material. However, micro-supercapacitors are facing some limitations in terms of energy density but also with device assembly because of the use of liquid electrolytes which lead to undesirable leakage. Solid state electrolytes are widely explored to improve the safety, to prevent leakage, and to help the assembly process. One interesting family of these solid electrolytes are confined ionic liquids, namely ionogels [2]. Ionogels, are particular electrolytes since they can be shaped as solids showing liquid-like behavior, regarding ions dynamics.

A simple way to improve the capacitance of a supercapacitor is to increase the accessible surface of each electrode on a given volume. The electrode surface can be expanded with 3D microstructures (such as hollow pillars as depicted on Figure a. [1]) and/or nanostructures (nanowires for example) to reach working area much higher than the footprint area of the electrodes.



Metal oxides such as MnO_2 exhibit fast redox mechanisms leading to pseudocapacitive behavior, and can be used in micro-supercapacitors when deposited as thin-film on highly conductive electrodes.

Ionic liquids are salts (such as 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid on Figure b.) that are liquid at room temperature. They show interesting characteristics, namely high ionic conductivity, high thermal and chemical stability and low vapor pressure, and can be confined in a solid matrix to form ionogels (see Figure c.). The electrochemical performance of ionogels are close to the corresponding ionic liquid ones. Depending on the binder material and the ions used, their mechanical and optical properties are tunable. Ionogels used herein, as well as their synthesis routes, have to be compatible with the nature and the architecture of the pseudocapacitive MnO_2 electrodes.

The confinement of the ionic liquid in an ionogel and the interactions between ionogels and the pseudocapacitive material will be studied through various characterization methods including Raman spectroscopy, infrared spectroscopy, electrochemical impedance, cyclic voltammetry, etc.

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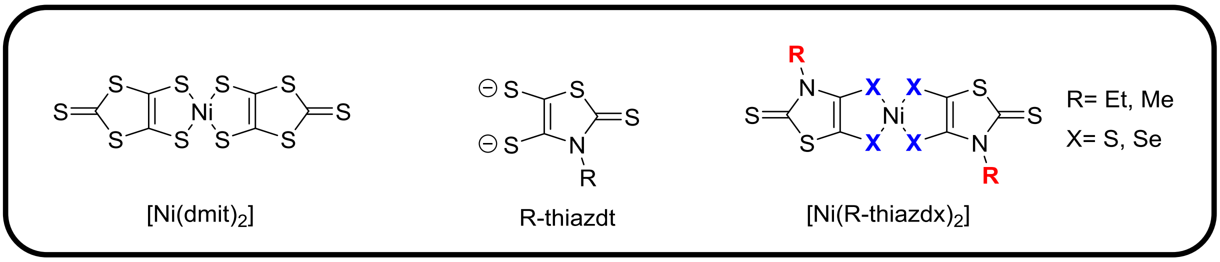
Single Component Conductors Based on Ni(R-thiazdt(s))$_2$ Complexes

Hadi Hachem[1], **Olivier Jeannin**[1], **HengBo Cui**[2], **Reizo Kato**[2], **Marc Fourmigué**[1], **Dominique Lorcy**[1]

[1] Univ Rennes 1, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, Campus de Beaulieu, Bât 10A, 35042 Rennes, [2] Condensed Molecular Materials Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan
e-mail: hadi.hachem@univ-rennes1.fr

Metal-*bis*(dithiolene) complexes have been intensively studied as precursors of multicomponent molecular conductors in mixed-valence salts and one prototypal complex within this class of molecules is the Ni(dmit)$_2$.[1] Another strategy is to use these complexes as precursors of single component molecular conductors, that is a neutral complex without any counterion. Highly conducting neutral nickel-*bis*(dithiolene) complexes bearing a non-innocent tetrathiafulvalene (TTF) backbone were successfully developed by Kobayashi et al.[2] So far, only two other examples of neutral Ni complexes lacking this TTF backbone and behaving as single component molecular conductors have been reported, namely the Ni(dmit)$_2$[3] and the [Ni(Et-thiazdt)$_2$].[4] Moreover the neutral complex Ni(dmit)$_2$ was recently shown to turn metallic under very high pressures.[3] Given these results and the structural flexibility provided by the (R-thiazdt) ligand, we decided to explore the synthesis of the methyl derivative [Ni(Me-thiazdt)$_2$], as well as the diselenolated complexes [Ni(R-thiazds)$_2$] (R=Me, Et), and observe the effect of these structural changes on the electronic, spectral, and transport properties of the complexes.



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Peptide Self-assembly polymorphism and pathways

Nadia Halzoun[1, 2], Enora PRADO[1, 3], Damien RAULT[1, 2], Cristelle MERIADEC[1], Franck ARTZNER[1*]
[1]Soft matter Department; [2]university of Paris Saclay, Paris France; [3]Ipsen Pharma, Dreux, France
**franck.artzner@univ-rennes1.fr*

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 interactions[1]. 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]. Peptide self-assemblies merge as attractive biomedical systems notably due to their biocompatibility, biodegradability[4].
In this presentation, a model of pharmaceutical peptide self-assemly is discussed. Triptorelin is a linear decapeptide which self-assembles into highly monodisperse small nanotubes in water (10% w/w). The impacts of pH and Temperature on the conformational change of the self-assemblies were investigated and a large polymorphism in supramolecular organisation has been shown(**Figure 1**)[5]. However, self-assembly mechanisms underlying this polymorphism remain misunderstood. The aim of my work was to determine the roles of pH and temperature on the conformational change. In this purpose, a multi-technics method was applied combining X-ray diffraction (SAXS and WAXS) and vibrational spectroscopies (Micro-RAMAN and ATR-FTIR).

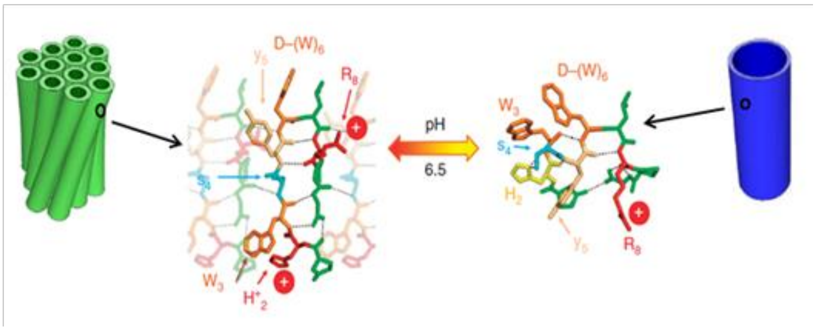

Figure 1: Representation of Triptorelin primary structure on the left and supramolecular organisation depending on the pH, on the right (small nanotubes in green, large ones in blue).
(Valéry, et al., 2015)

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SYNTHESIS AND ELECTROCHEMICAL STUDY OF MIXED-VALENCE TRIIRON CLUSTERS DERIVED FROM DINUCLEAR MODELS OF THE ACTIVE SITE OF [Fe-Fe] HYDROGENASES

A. HOBBALLAH [1*], **C. ELLEOUET** [1], **F. PETILLON** [1], **P. SCHOLLHAMMER** [1]

[1]*CNRS, CEMCA (Laboratoire de Chimie Electrochimie Moléculaires et Chimie Analytique), Faculté*
des Sciences et Techniques - 6 Avenue Victor le Gorgeu, CS 93837
29238 Brest, France Cedex3
**Ahmad.hobballah@univ-brest.fr*

The structural determination of [Fe-Fe]-hydrogenases has led during the two last decades to the reinvestigation and a huge development of iron carbonyl thiolate complexes chemistry.[1] The use of well-known organometallic tools has allowed to reproduce some chemical and structural precedents of the natural site which have contributed to a better understanding of the chemistry of the H-cluster.[1] During these studies, very original side products featuring quasi linear tri- and tetranuclear arrangements have been synthesized.[2] These novel polynuclear complexes do not model directly the H-cluster of the [Fe-Fe]-hydrogenases but their chemistry is related.

Some years ago, the unexpected formation of the trinuclear, mixed valence {Fe(I)Fe(II)Fe(I)} species, $[Fe_3(CO)_5(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})_2]$ ($P^{Ph}{}_2N^{Ph}{}_2$ = $(PPhCH_2NPhCH_2)_2$; pdt = propanedithiolate) was reported as a side product, from the reaction between $[Fe_2(CO)_6(\mu\text{-pdt})]$ with $P^{Ph}{}_2N^{Ph}{}_2$ through a non-established mechanism.[3] The reminiscence of the original structure of this compound with mixed valent Fe(I)Fe(II) systems and the possible efficient activity, as electrocatalyst towards H^+/H_2 conversion, of such trinuclear compounds led to define a general route to elaborate this class of derivatives which can be considered formally as constituted by the combination of a diiron framework and a mono iron moiety as a metalloligand.[4]

This communication will present the extension of this strategy for the preparation of a series of novel triiron complexes $[Fe_3(CO)_5(\kappa^2\text{-dppe})(\mu\text{-dithiolate})(\mu\text{-pdt})]$ with different dithiolate bridges in order to tune their electronic and steric properties. Their spectroscopic characterizations and their electrochemical properties will be presented.

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Influence of mesoporous or parasitic $BiFeO_3$ structural state on the magnetization reversal in multiferroic $BiFeO_3$ /$Ni_{81}Fe_{19}$ polycrystalline bilayers

W. Jahjah[1], J.-Ph. Jay[1], D. T. Dekadjevi[1], Y. Le Grand[1], A. Fessant[1], J. Richy[1,2], B. Warot-Fonrose[2], A. R. E. Prinsloo[3], C. J. Sheppard[3], D. Spenato[1]

[1] OPTIMAG – EA 938 – UBO/UBL – 6, avenue le Gorgeu 29200 Brest.
[2] CEMES CNRS-UPR 8011, Université de Toulouse, 31055 Toulouse, France
[3] Cr Research Group, Department of Physics, University of Johannesburg, South Africa.
e-mail : walaa.jahjah@univ-brest.fr

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, $BiFeO_3$ (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 *He*, and by an enhancement of the coercive field *Hc*. Room-temperature exchange bias has already been demonstrated in epitaxial BFO/FM [7], as well as in polycrystalline thin films.[8]

We report through a systematic experimental study on the direct correlation between the Bi_2O_3 parasitic phase concentration that crystallizes in the BFO and the magnetic properties of the polycrystalline heterostructure BFO/FM=$Ni_{81}Fe_{19}$ deposited via magnetron sputtering. We find that the macroscopic *He*, that arises from exchange bias coupling, is null for phase-pure BFO, and increases up to 18 Oe with an increasing concentration of Bi_2O_3. 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.

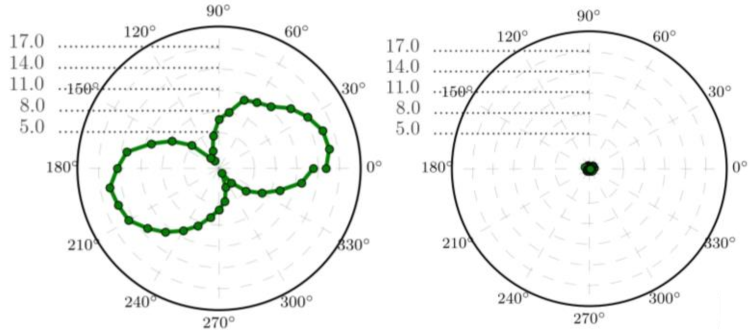

Fig. 1: Azimuthal evolutions of *He* (in *Oe)* in BFO/NiFe for BFO with (left) and without (right) parasitic phases.

These results show for the first time the role of the usually known defects in the BFO/NiFe bilayer (i.e. the parasitic phase Bi_2O_3 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] This work was recently published in *Journal of Applied Physics.*[10]

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TOLUENE/BUTANOL BINARY SOLVENTS CONFINED IN PERIODIC ORGANOSILICATES: NEW INSIGHT FROM NEUTRON DIFFRACTION STUDIES.

Aicha JANI, Benedikt MIETNER, Viviana CRISTIGLIO, Patrick HUBER, Michael FRÖBA, Denis MORINEAU

The confinement of liquid mixtures in porous channels provides new insight into fluid ordering at the nanoscale. In this presentation, we address a phenomenon of microphase separation, which appears as a novel fascinating confinement effect for fully miscible binary liquids. This phenomenon was firstly investigated for tert-butanol-toluene mixtures confined in the straight and mono-dispersed cylindrical nanochannels of MCM-41 and SBA-15 mesoporous silicates (D = 3.6 nm and 8.3 nm) [1,2].
The present study aims at extending this approach to different fluid-wall interactions. It shows that novel types of nanostructures can be generated using functionalized porous organosilicates with periodic alternating surface chemistry along the pore channel.

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Chalcogenide photonic integrated platform for near- and mid-infrared applications

N. Jebali[1], E. Delcourt[2], L. Bodiou[3], V. Nazabal[4], J. Charrier[5], Y. Dumeige[6]

[1]Univ Rennes, Institut FOTON, UMR-CNRS 6082, BP80518, F-22305 Lannion Cedex, France
[2]CNRS UMR 6226 ISCR, Université Rennes, 35042 Rennes, France
**e-mail: nessim.jebali@univ-rennes1.fr*

Chalcogenide glasses have raised tremendous attention in recent decades due to their unique optical properties, which make them promising candidate materials for the development of a wide range of photonic applications [1]. In particular, all-optical processing in near-infrared telecommunication window is taking advantage of their high optical nonlinearities. These glasses also exhibit low maximum phonon energies which yield broad transparency window from visible to mid-infrared wavelength ranges. Optical sensing platforms could therefore also benefit from the development of these materials [2].

Relying on previous experimental results obtained in our laboratory that demonstrated cascaded four-wave mixing using chalcogenide micro-resonators, we aim at developing and studying waveguides and coupled optical micro-resonators made of chalcogenide glasses.

On the one hand, we are studying dispersion optimized GeSbSe waveguides to obtain a supercontinuum in the mid-infrared spectral range. On the other hand, we are carrying out research on the dynamical properties of coupled nonlinear micro-resonators to obtain all-optical oscillations in the range 10-40 GHz [3]. Moreover, the resonance frequency splitting of coupled resonator system could be used to obtain Brillouin scattering under doubly resonant for both the pump and the Stokes waves.

The poster will focus on the theoretical part of this project. We will also present the simulations results obtained regarding the design of different structures (waveguides and ring-resonators) obtained by the use of a mode solver based on the finite difference methods.

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Tunable coherent sources for sensors or telecom applications

Amith Karuvath, Pascal Besnard* (A. Karuvath, P. Besnard)

Univ Rennes, CNRS Institut FOTON, 6 rue de Kerampont, CS 80518,22305 Lannion, France
**e-mail : (pascal.besnard@enssat.fr)*

My thesis project has several goals:

- Realization of a tunable source in the C-band (1530-1560 nm) with sub-kHz linewidth.
- Study of the synchronization process of optically-injected single- and multi-frequency lasers [2,3] in terms of intensity and frequency noise [4,5].
- Exploration of the sensitivity limits using selective coherent amplification [6]: detection at the attowatt level of a continuous-wave at room temperature.
- Detection of a few photons by selective optical amplification [7].

We have demonstrated the concept of sub-kHz tunable source in the laboratory, and are now attempting to gain a better understanding of its properties, prospects and limitations. This type of source can potentially allow significant advances from a scientific and industrial point of view in areas including instrumentation, and sensors. We have so far been able to show the possibility of detecting, by selective coherent amplification, continuous wave signals at the femtowatt level at room temperature (or 100 photons for a discontinuous wave) [6,7]. The project will push these limits forwards, which opens perspectives for the realization of sensors of very high sensitivity or for highly coherent comb of modes that can be used in optical communications.

Other objectives accompany this thesis work: improvement of phase noise detection using nonlinear optics; simulation and theory of the behaviour of coherent laser sources.

We will detail in this presentation the interest of tunable source for selective amplification and the study of synchronization process from a general point of view.

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Synthesis of amphiphilic compounds by click chemistry

M. Khalil[1]*, M. Berchel[1], P-A. Jaffrès[1]

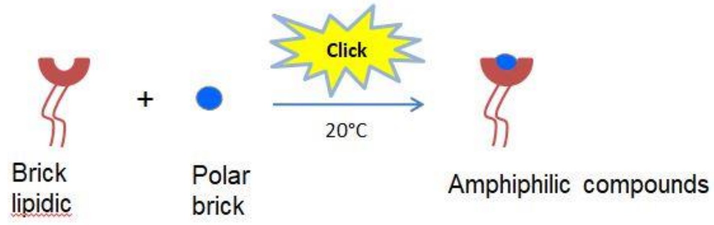
[1]UBO, UMR-CNRS 6521 « Chimie Electrochimie Moléculaire et Chimie Analytique » 6 Avenue Victor Le Gorgeu, 29238 Brest

**e-mail: Montassar.Khalil@univ-Brest.fr*

Amphiphilic compounds are molecules that have simultaneously a hydrophobic part which is usually a lipidic chain and a hydrophilic part that determines to which family they belong. They can be ionic (cationic, anionic and gemini) or neutral. Cationic amphiphiles are used to carry nucleic acids (pDNA, RNA) and open new possibilities for gene therapy. Previous studies have been conducted to synthesize amphiphilic compounds in our laboratory and some were obtained by using click reaction. To this respect, we can mention the synthesis of fluorescent amphiphiles prepared by click reactions (alkyne/ azide[1,2] or thiol-ene[3,4]) These click reactions have the advantage of being simple to conduct, easily purified with a good tolerance to many conditions and good yields.

The purpose of this study is to design new amphiphilic species (cationic or fluorescent) prepared by new type of click reaction. The goal consist to prepare lipid building unit featuring two lipid chains that could react at room temperature and potentially in water, with a polar head group to produce instantaneously an amphiphilic compound. The first part of this study is therefore methodologic to prepare the lipid building block and to study the click reaction to produce amphiphilic compounds.

Basically, the goal of this project can be summarized as schematized below.



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SYNTHESIS STRATEGY FOR CYCLAM-DERIVATIVES COBALT-COMPLEXES ABLE TO MODULATE AMYLOID-B AGGREGATION

E. Lelong, H. Bernard, R. Tripier

Université de Bretagne Occidentale, UMR-CNRS 6521, UFR Sciences et Techniques, 6 avenue le Gorgeu, 29200 BREST, Fance
evan.lelong@univ-brest.fr

Alzheimer's disease (AD) is the most common form of dementia in humans.[1] Amyloid-β peptides (Aβ) have been admitted as central cause in neurotoxicity pathway of AD.[2] Aβ self-assembles into fibrillary structures which induce neuroinflammation, oxidative stress, and lead to cellular death.[2] Recently, the use of metal-complexes able to modulate Aβ aggregation offers new opportunities in chemistry research field.[3] Unfortunately, little has been reported to pursue this strategy. To our knowledge, only one cyclam derivative Co(II)-complex, $[Co(II)(TMC)]^{2+}$, has been recently reported to induce Aβ hydrolysis (Figure 1).[4] The mechanistic hypothesis of peptide bond hydrolytic cleavage involves hydroxyl group generated, thanks to the properties of cobalt center. This coordinate hydroxide forms a metal-hydroxo complex, which can directly react with amide bond or generate another hydroxide from bulk water.

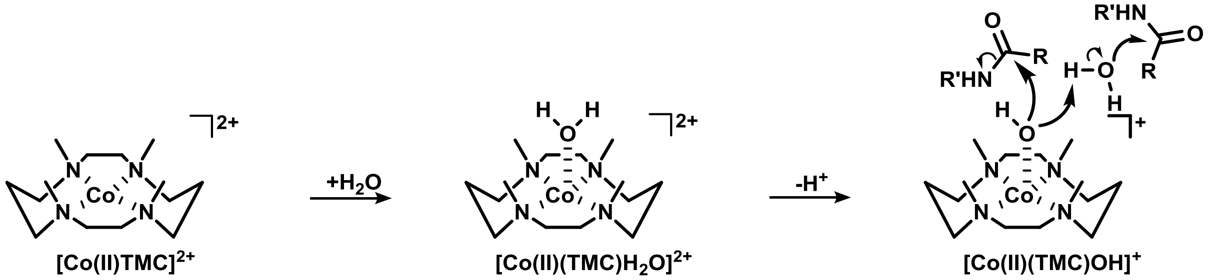

Figure 1. Hypothesis of hydroxide generation for peptide hydrolysis.

Considering these hypotheses, it is likely to imagine an alcohol function on the macrocycle backbone, which could offer similar effects on bulk water deprotonation than metal-hydroxo complex. Alcohol arm could be introduced on the macrocycle carbon backbone using a method of *C*-functionalization recently developed in our lab, or on a nitrogen atom through regiospecific alkylation.[5] In order to understand how structures can impact properties of cobalt-complexes, series of methylated and cross-bridged cyclams bearing one ethanol arm have been targeted (Figure 2). We will present full controled synthetic pathways to obtain these *C*-functionalized or *N*-functionalized cyclam derivatives.

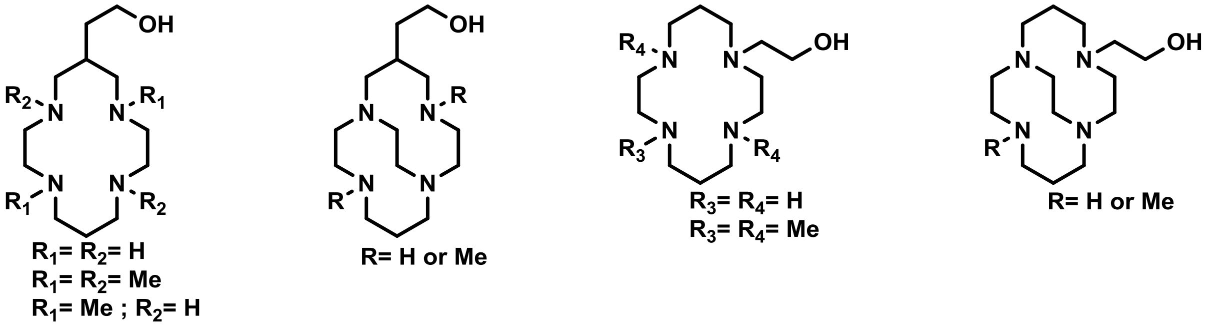

Figure 2. Structures of targeted cyclam-derivatives

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PROBING THE ULTRAFAST RESPONSE OF BI_2TE_3 INDUCED BY NEAR-IR AND THZ FEMTOSECOND PULSES

A. Levchuk[1], V. Juvé[1], G. Vaudel[1], M. Weis[1,2] and P. Ruello*[1]

[1]Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans Université
avenue Olivier Messiaen, 72085 Le Mans, France
[2]A. Chelkowski Institute of Physics and Silesian Center of Education and Interdisciplinary Research,
75 Pulku Piechoty 1A University of Silesia, 41-500, Chorzów, Poland

**e-mail: pascal.ruello@univ-lemans.fr*

Topological insulators (TI), as a new type of materials may lead to developments in magnetoelectronics, spintronics and quantum computing due to their unique physical properties [1]. Small insulating bulk bandgap (around 0.3 eV [2]) and conducting spin-polarized surface states that are protected against superficial deformations and impurities by topological means, made TI widely discussed and investigated topic over the last few years [3]–[5].

Despite the high scientific interest, the way to probe selectively only these topologically protected surface states remains challenging. Small bandgap, quantum well states in forbidden energy band as well as complicated band structure pushes forward the research into developing new materials with TI like properties. Nevertheless, understanding the light-matter interaction mechanisms in TIs is one of the scientific areas of interest. Up to this point, only ARPES can directly access the Dirac surface states [6]. For example, it could be possible to evaluate the contribution of these unique surface states by investigating the variation of the TI's optical response, induced either by THz or optical pumping.

We performed the pump-probe measurements with a sub-picosecond time resolution on the set of Bi2Te3 samples grown by the state-of-the-art MBE technique [7]. TI films were irradiated by femtosecond pulses with a central wavelength of 800 nm (375 THz/1.54 eV) and 600 µm (0.5 THz/2 meV) and probed at 400 nm (749.5 THz/3.1 eV). Hereby we report that there are no apparent differences in the sample's photoinduced response between 800 nm and 0.5 THz pumping. Therefore, initial Bi2Te3's excitation and presence of a Raman-active A_{1g} optical phonon for both Near-IR and THz irradiation could be attributed to different physical mechanisms which are to be discussed here.

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Er3+-doped Ga-Ge-Sb-S glass thin films by PVD deposition

G. Louvet1,3, E. Baudet2,3, S. Normani2, F. Starecki1,4, P. Camy4, M. Bouška2, J. Gutwirth2, P. Němec2, C. Cardinaud5, C. Calers5, Y. Ledemi3, A. Douaud3, S.H. Messaddeq3, L. Bodiou6, J. Charrier6, J.L. Adam1, Y. Messaddeq3, V. Nazabal1,2

1 Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226 CNRS, Université de Rennes 1, 35000 Rennes, France;

2 Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic;

3 The Center for Optics, Photonics and Lasers (COPL), Laval University, Quebec, QC G1V 0A6, Canada;

4 Centre de recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen, 14050 Caen, France;

5 Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 44322 Nantes, France

6 FOTON UMR-CNRS 6082, Université de Rennes 1, ENSSAT BP80518, Lannion, F22305, France

**e-mail: geoffrey.louvet@univ-rennes1.fr*

In the frame of the major issues related to global warming and pollution, the microsensor based on mid-infrared (MIR) spectroscopy is a useful tool to allow continuous measurement of different bio-chemicals species that disturb our environment.

In the aim of developing a MIR source potentially integrated in a microsensor, we fabricated rare earth doped chalcogenide thin films by different phase vapor deposition (PVD) technics. The RF magnetron sputtering, pulsed laser deposition (PLD) and electron beam evaporation were investigated. The selected glass system is Ge-Ga-(Sb)-S with Er^{3+} ions doping. Er^{3+} ions show emissions in NIR and MIR at 1.55 µm ($^4I_{13/2}\rightarrow{}^4I_{15/2}$) and at 2.8 µm ($^4I_{11/2}\rightarrow{}^4I_{13/2}$) under excitation at 808 nm. Deposition parameters were optimized for the three PVD techniques based on a comparison to define the higher fluorescence efficiency. Sulphide thin films were characterized by means of transmission, AFM, XPS, SEM, EDS, ellipsometry and Raman spectroscopy to better control the deposition behavior.

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A layered double perovskite: In situ exsolution and integration of transition metal nanoparticles as a catalyst for efficient SOFC anode

Praveen Managutti[1], **Mona Bahout**[1], **Olivier Hernandez**[1], **Carmelo Prestipino**[1],
Svetlana Tsareva[2], **Serge Paofai**[1]

[1] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France*

[2] *Univ Rennes, CNRS, ScanMAT (Synthèse Caractérisation ANalyse de la MATière) - UMS 2001, F-35000 Rennes, France*

praveen.managutti@univ-rennes1.fr
pmanagut@insa-rennes.fr

In Solid oxide fuel cell (SOFC), anode directly exposes the catalyst to fuels. Currently, Ni/YSZ cermet is the state-of-the-art SOFC anode material, due to its high electrical conductivity, excellent electrocatalytic performance towards fuel oxidation, high mechanical strength and low cost. Despite these advantages, Ni-cermet anodes exhibit several limitations including Ni sintering at high temperature, redox instability and coarsening [1, 2], deactivation under direct hydrocarbon fuel cell operation due to carbon deposition and sulfur poisoning. Various efforts have been devoted to overcome the above problems, *e.g.*, by replacing the cermet with alternative anode materials such as perovskite oxides [3,4]. Although some materials are stable under the anode atmosphere and demonstrate coking tolerance for hydrocarbon fuels, cell performance is generally much lower than that obtained with Ni-cermets due to insufficient catalytic activity and electrical conductivity making them inadequate for practical applications. The layered double perovskite manganite, $PrBaMn_2O_{5+\delta}$, has been proposed as potential anode for SOFC [5,6]. However, the ionic conductivity is low and does not sustain a good catalytic activity, despite the promising results in terms of stability, compatibility with electrolyte (LSGM) or sulfur poisoning [7]. A novel approach towards the surface functionalization is the preparation of nanostructured particles, directly from a host matrix, which can occur under change of operating conditions [10]. Exsolution of transition metals on the surface of perovskites has been proposed as a smart catalyst design for SOFCs' anode because of the potential enhancement in electrochemical activity, preventing metal agglomeration and coarsening under processing and operation conditions [8]. Recently, the layered perovskite manganites, LnBaMn 2 O 5+δ (Ln = Pr, Nd) which are stable under reducing conditions have been proposed as potential anode for SOFC [5,6].Although they demonstrate coking and sulfur tolerance for hydrocarbon fuels, cell performance is much lower than that obtained with Ni-cermetsdue to insufficient catalytic activity making them inadequate for practical applications. To solve this problem, small quantities of very active nanoparticles, e.g., Ni or Ru, can be added by impregnation of a pre-sintered conducting electrode with a metallic salt or a nanopowder suspension. Because the impregnation method can result in a non-homogeneous distribution of metallic particles and grain coarsening during the high temperature thermal treatments required for cell preparation, we used the alternative exsolution method to introduce efficient catalysts in the layered perovskites, PrBaMn2-xNixO5+δ ($0.05 \leq x \leq 0.3$) synthesized by our group. In situ precipitation of the Ni nanoparticles at the surface of the layered oxide was carried out under humidified (3% H 2 O) H 2 /Ar at 875 °C. This samples are prepared by synthesized using pechini method and characterized by means of powder X-ray diffraction (a), thermogravimetry (b), scanning electron microscopy (c).

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C-FUNCTIONALIZED 1,4,7-TRIAZACYCLONONANE (TACN) SYNTHESIS FOR BIFUNCTIONAL CHELATORS FOR POSITRON EMISSION TOMOGRAPHY IMAGING

Axia MARLIN[1*], **Véronique PATINEC**[1], **Raphaël TRIPIER**[1]

[1]UBO, UMR-CNRS 6521 « Chimie Electrochimie Moléculaires et Chimie Analytique », 6 Avenue Victor Le Gorgeu 29238 Brest
[*]email : axia.marlin@univ-brest.fr

Positron Emission Tomography (PET) is a nuclear technic for tumors imaging which involves the in vivo injection of a radiopharmaceutical that requires β^+ emitting radionuclides. When the radionuclide is a metallic cation, it needs to be introduced in an encapsulated chelate form to avoid the release of the radioactive element in the body. Cyclic polyamines as 1,4,7-triazacyclononane (TACN) are often used as chelators because of their abilities to form stable complexes with transition metal cations. Some of TACN-based chelators were already studied in our group for copper-64 complexation for PET imaging [1-3].

In order to target tumor cells or a specific physiological event, these chelators have to be extended to their bifunctional analogues. In other words, the triazamacrocyclic skeleton possesses coordinating functions for the metal cation chelation as well as a grafting function allowing the conjugation with biomolecule of interest (antibody, peptide…) that will target the tumor. One of the most used way for TACN-based bifunctional chelators preparation is to introduce the grafting function onto a nitrogen atom by *N*-functionalization or onto one of the coordinating arms. However, the synthesis of such chelators requires many steps and needs to be adapted for each considered chelators. Moreover, it was demonstrated that the loss of a coordinating arm could cause stability lost and kinetic inertness decrease [4]. To overcome these problems, an approach consists of introducing the grafting function onto a carbon atom of the macrocycle by *C*-functionalization, in that way the nitrogen atoms remain available for further introduction of coordinating arms (Figure 1). Thus, a bioconjugable platform on which different coordinating arms can be introduced is obtained, which gives access to a wide variety of bifunctional chelators.

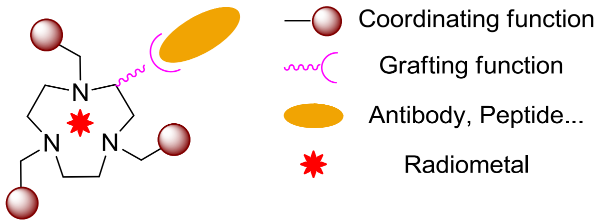

Figure 1 : Radiopharmaceutical based on C-functionalized TACN bifunctional chelators

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HETEROMETALLIC CLUSTERS [RE6-XMOXSE8(CN)6]N- (X = 1–3): PREPARATION AND PROPERTIES OF THE COMPOUNDS WITH DIFFERENT RE/MO RATIO

V.K. Muravieva[1,2]*, Y.M. Gayfulin[1], N.G. Naumov[1,3], S. Cordier[2]

[1]Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, 630090, Russia, [2]Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), Rennes, F-35000, France, [3]Novosibirsk State University, 2, Pirogova str., Novosibirsk, 630090, Russia

**e-mail: viktoria.muravyeva@univ-rennes1.fr*

Octahedral transition metal cluster complexes are relevant building blocks for the material design due to their intrinsic properties, rigid geometry and stability of the core [1, 2]. Physical and chemical properties of the cluster core are driven by the electronic structure, or more precisely, mutual location and energy of frontier orbitals combined mostly of the core atoms of the cluster. Non-isovalent metal substitution should influence significantly on electronic structure and cluster properties. However, mixed-metal cores $\{M_{6-x}M'_xQ_8\}$ can be achieved only at the preparation stage, resulted in the complex product mixture [3, 4].

Here we present the synthetic strategy for the preparation of the heterometallic cluster complexes $[Re_{6-x}Mo_xSe_8(CN)_6]^{n-}$ (x = 1-3) as individual compounds. We demonstrate that intrinsic characteristics of the complexes with different metal ratio in the core can be used to separate clusters with the same geometry and ligand environment. Cluster complexes $[Re_3Mo_3Se_8(CN)_6]^{4-}$, $[Re_4Mo_2Se_8(CN)_6]^{4-}$, $[Re_5Mo_1Se_8(CN)_6]^{4-}$ were prepared and characterized. Different ratio of non-isovalent metal atoms in the cluster core was found to influence strongly on electronic structure, the spectroscopic characteristics and redox properties of the resulting cluster. Crystallographic study of isostructural compounds $TBA_4[Re_{6-x}Mo_xSe_8(CN)_6]$ (x = 1-3) obtained revealed the increase in the average M-M distances (M = Re, Mo) during Re substitution for Mo in the cluster core (Figure 1).

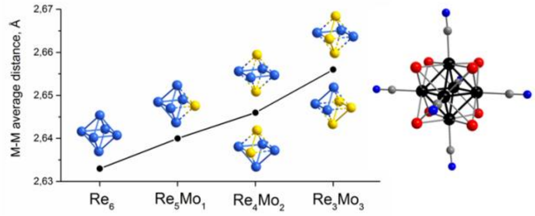

Fig. 1: Average M-M distances in the cluster salts $TBA_4[Re_{6-x}Mo_xSe_8(CN)_6]$, x = 1-3 (left), the common structure of $[Re_{6-x}Mo_xSe_8(CN)_6]^{4-}$ anion in salts obtained (right).

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LTCC KU-BAND CIRCULATORS

N. PARKER-SOUES[1]

[1]*Université de Bretagne Occidentale, Avenue Le Gorgeu, Brest*
norbert.parker@univ-brest.fr

Circulators are one of the main components for microwave applications. They are based on the inclusion of a ferrimagnetic material inside a dielectric between a 3-port conductive junction and a ground plane to create a rotation of the electromagnetic waves from one port to another, therefore isolating the third port. However, their cost is high and their integration can be complicated. These are two reasons of the continuing research on the subject and the main motivation for the PhD this poster aims to contextualize.

The need for the *Direction Générale de l'Armement* (DGA) is to replace mechanically steered antennas with electronically steered ones by integrating a high number of surface mounted devices (SMD) circulators while keeping the cost down. To do so, the LTCC technology will be used. It and the different opportunities it offers[1 are showcased in the poster. My PhD follows a previous one and the LOCCIMIM project[2], whose state-of-the-art results are presented as well, and is combined with the ASTRID CirCKu project.

By the end of this PhD and in association with the CirCKu project, we aim to answer both the DGA and spatial needs in the Ku-Band with suitable performances for both of the usages.
The development of the LTCC technology within the Lab-STICC shall allow us to bring other types of ferrimagnetic based components to this technology or try-out new architectures only available through a LTCC realisation.

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SYNTHESIS OF NOVEL FLUORESCENT TETRACYANOBUTADIENES TOWARDS NEW AIE FLUOROPHORES

C. Philippe[1*], **L.Lemiègre**[1], **Y.Trolez** [1]

[1]*Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7*
**e-mail: clotilde.philippe@ensc-rennes.fr*

Since 1999, the sequence of [2+2] cycloaddition followed by a [2+2] retroelectrocyclization (CA-RE) between tetracyanoethylene (TCNE) and organic electron-rich alkynes leading to tetracyanobutadienes (TCBDs) is well known.[1] Lots of electron-donating groups (EDG) have now been tested with success, allowing this CA-RE to be a new efficient « Click Reaction ». [2] Ynamides, whose synthesis was optimised by Hsung group [3] and Evano group [4], were demonstrated to have great reactivity with TCNE at room temperature by our group in 2014. [5] The nitrogen atom is acting as an electron-donating group. (Figure 1)

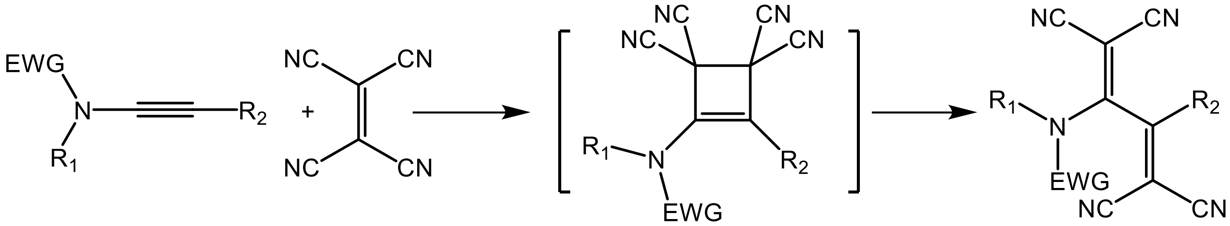

Figure 1: CA-RE of TCNE with ynamide
EWG: Electron-withdrawing group

The influence of R_1 and R_2 was investigated and showed that R_1 has little impact on reactivity, whereas R_2 allows the preparation of TCBDs with a wide range of optical properties.[6] The possibility to tune their optical properties is a major contrast with previously reported TCBDs. It was also recently found that these TCBDs can be fluorescent at room temperature in the solid state and not in solution. It meens that certain TCBDs from ynamide can be Aggregation-Induced Emission (AIE) molecules. It is an unusal behavior compared to common fluorescent molecules, which are highly fluorescent in diluted solution and less (or not) fluorescent when concentrated or in the solid state due to Aggregation-Caused Quenching (ACQ, π-stacking that quenches the emission properties).
The aim of this project is then to synthesize novel TCBDs and especially AIE molecules, which can be used for various applications in biophysics for example.

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Influence of donor and acceptor substituents on photoinduced optical birefringence in novel thiophene derivatives

Anna Popczyk[1,2], **Jaroslaw Mysliwiec**[1], **Yohan Cheret**[2], **Abdelkrim El-Ghayoury**[2], **Bouchta Sahraoui**[2]

[1] *Wroclaw University of Science and Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland*
[2] *University of Angers, CNRS UMR 6200, MOLTECH Anjou Laboratory,*
2 Bd Lavoisier,49045 Angers Cedex, France
E-mail address: anna.popczyk@pwr.edu.pl

Optoelectronics and photonics are developing branches of science which require new concepts, technologies and materials. Search for new materials with unique optical and electrical properties, possessing at the same time interesting nonlinear optical properties is a challenge. Research are focused on organic compounds, mostly because of their price, non-complicated methods of production and easy way of recycling. Derivatives of thiophene are very promising organic materials for advanced technologies[1]. Synthesized molecules are typical representatives of push-pull organic chromophores and their structure is schematically presented in Fig 1. As a donor we used tetrathiafulvalene (TTF) or benzothiophene (BT), whereas as an acceptor - nitrobenzene and benzonitrile were chosen. All four compounds were prepared under Wittig-Horner conditions. Structure of donor and acceptor parts have a crucial impact on intramolecular charge transfer and linear, as well as nonlinear optical properties [2]. Abovementioned compounds were embedded in polymer matrix (PMMA) to achieve host/guest systems.

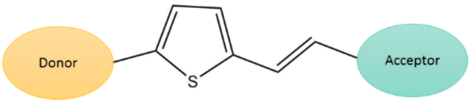

Fig. 1 Scheme of investigated structures

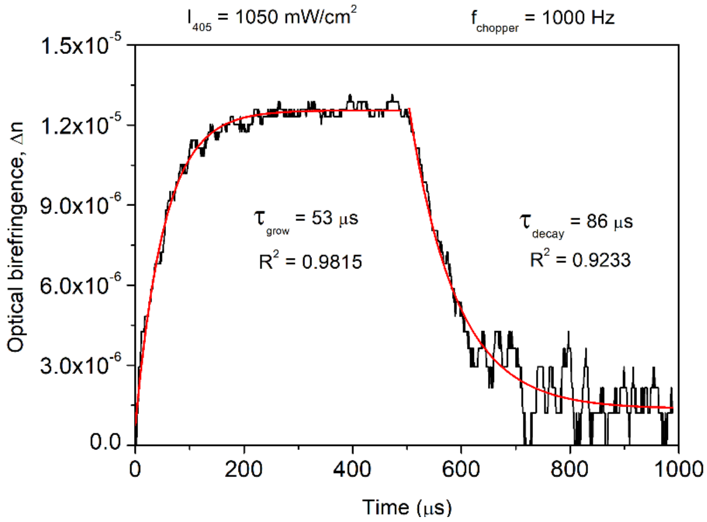

Fig. 2 Dynamic photoinduced birefringence of TTF-TPh-pCN

In order to estimate the photoinduced birefringence in fabricated thin films, we used experimental setup for optical Kerr effect (OKE) [3]. This method allowed us to observe kinetics of induced anisotropy, including dynamic and static change of refractive index, along with signal growth and decay. Experimental results show fast (in order of microseconds) and efficient dynamic photoinduced birefringence. Exemplary result of dynamic change of Δn is presented in Fig 2. Additionally, we calculated the third-order susceptibility ($\chi^{(3)}$) and nonlinear refractive index coefficient (n_2).

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Isolation and characterisation of hydroxyproline-rich glycoproteins from green macroalga *Ulva lactuca*

T. Prerovska*[1,2], P. Lipovova[1], V. Ferrieres[2], E. Nguema-Ona[3]

[1]UCT Prague, Technická 5 166 28 Praha 6, [2]ENSC Rennes, 11 Allée de Beaulieu, 35708 Rennes,
[3]Centre Mondial de l'Innovation Roullier, 18 Avenue Franklin Roosevelt, 35400 Saint-Malo
**e-mail: tprerovska@gmail.com*

Hydroxyproline-rich glycoproteins (HRGPs) encompass a large and complex group of cell wall proteins distributed throughout the plant kingdom with various form and function. [1][2][3] HRGPs have been and remain the subject of several studies, particularly in higher plants, because they were reported to play an essential role in many aspects of plant growth and development including embryogenesis, cell growth, and differentiation, in plant defense responses to biotic and abiotic stress, as well as in sexual reproduction. [4][5][6] Based on their structure are HRGPs usually categorized into i) non-glycosylated or minimally glycosylated proline-rich proteins (PRPs), ii) moderately glycosylated extensins (EXTs) and iii) highly glycosylated arabinogalactan-proteins (AGPs). However, with increasing data available it is obvious that this family comprises a continuum of molecules, since substantial number of chimeric and hybrid HRGPs was described. [1]

Unfortunately, all so far known general group characteristics are based on research in land plants and little is known about their occurrence, structure, and function in algae. The biggest obstacle is missing genetic information on most of the macroalgal species, so the genomic analysis based on well described motifs of each group and amino acid bias cannot be used. Thus the main tools to study these proteins in algae are monoclonal antibodies (Jim and LM series) developed against HRGPs, together with Yariv reagents (synthetic phenylazo dyes, which react positively with AGPs). [7][8]

Ulva species are one of the most abundant representatives of Ulvophyceae, the main multicellular branch of the Chlorophyceae, which are ubiquitous in coastal benthic communities around the world. [9] Recently in order to understand marine ecosystems was the whole-genome sequence of *Ulva mutabilis* published, which makes *Ulva mutabilis* the first fully-sequenced green seaweed. [14] Up to now was the research of *Ulva* species mainly focused on dietary characteristics or polysaccharide composition with highlight to ulvan, which has been reported to exhibit wide range of biological and physiological activities. [10][11][12] So far there is no experimental information about localisation and structure of cell wall proteins, particularly hydroxyproline-rich glycoproteins, in *Ulva lactuca*. The only two studies mentioning their presence in *Ulva* species based on genomic analysis are Stanley et al. and Clerck et al. [13][14]

We confirm the presence and show the localization of AGP and EXT-like motifs within the cells walls of *Ulva lactuca* based on the fluorescence microscopy with JIM16 and JIM20 primary antibodies with specificity to land plant AGPs and EXTs. In the case of AGPs was their presence confirmed also by Yariv reagent. We were able to extract and purify AGPs, but not EXTs, which seems to be crosslinked in the cell walls. Characterisation of extracted AGPs as well as further attempts to extract EXTs are ongoing.

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Performance improvements of a nematic liquid crystal dichroic dye mixture by addition of a chiral dopant

<u>K. Raimondeau</u>[1], L. Dupont[1], JL. de Bougrenet de la Tocnaye[1]

[1]Optics Department, IMT Atlantique Bretagne-Pays de la Loire, Technopôle Brest-Iroise CS 83818
29238 Brest cedex 03 France
**e-mail: kevin.raimondeau@imt-atlantique.fr*

Abstract :

Switchable polarizers can be made by combining liquid crystal materials with dichroic dyes. This work presents a way to improve the dichroic ratio and switching response time of a nematic liquid crystal combined with a black dichroic dye mixture in a thin cell (2µm). The need for large dichroic ratio and fast switching time is often required to provide fast polar-free shutters. In practice, we cannot increase the dichroic dye concentrations in the mixture without observe some demixing phenomena so we have to investigate other ways to improve the dynamic performance. A solution is to add a small concentration of chiral dopants, with a small helical power around some mass percentage in the mixture. We present here some experimental results showing the impact of the addition of this chiral dopant on both dichroic efficiency and switching time, for two commercially available liquid crystal mixtures. In parallel, we investigate the steady and transient liquid crystal structure states because supposed to introduce residual scattering, incompatible with some applications requiring a high optical quality. This enables to establish a link between the presence of a progressively forming twisted structure and a fully established cholesteric one exhibiting a Bragg mirror in the visible range, as a function of the chiral dopant concentration.

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Etudes par électrochimie et spectrométrie de masse d'un catalyseur $[Cu(bpy)]^+$/TEMPO pour l'oxydation de l'alcool benzylique en benzaldéhyde.

M. Regnacq*[1], **F. Gloaguen**[1], **N. Le Poul**[1], **A. Memboeuf**[1]

[1]UMR 6521 CEMCA, Faculté des Sciences et Techniques - 6 Avenue Victor le Gorgeu, 29238 BREST
**e-mail: matthieu.regnacq@univ-brest.fr*

La synthèse des aldéhydes à partir d'alcools correspondants, a été largement étudiée [1],[2],[3]. Les aldéhydes sont essentiellement utilisés en parfumerie ou dans le domaine de l'énergie. L'oxydation des alcools benzyliques et dérivés en aldéhydes peut être réalisée de manière efficace par le complexe $[Cu(bpy)]^+$ en présence de TEMPO et de dioxygène (bpy = bipyridine, TEMPO = (2,2,6,6-tétraméthylpipéridin-1-yl)oxy). Différentes propositions mécanistiques ont été proposées dans le cas de cette synthèse aérobie.[4],[5] Récemment, une étude novatrice s'est penchée sur l'oxydation électrochimique des alcools en l'absence d'oxygène (Fig. 1).[6] La nature et la concentration des différentes espèces (alcool, base, co-catalyseur) ont été variées afin d'optimiser le rendement de la réaction. Cependant, le mécanisme anaérobie n'a pas été déterminé.

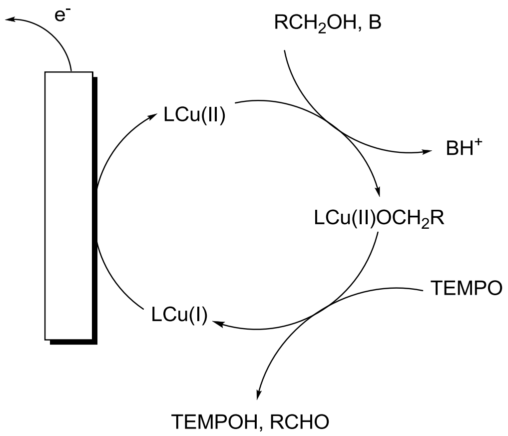

Figure 1 : Séquence envisagée pour l'oxydation des alcools (L=bipyridine, B=base, R=Ph p-substitué, H, Me, OMe, Br, CF_3, NO_2).

Dans ce contexte, nous avons réalisé des études expérimentales afin d'obtenir une description plus précise du mode de fonctionnement de ce système catalytique et de pouvoir l'améliorer en conséquence. Le solvant, la base et le ligand L (L = éthylènediamine, bpy fonctionnalisées, phénantroline) ont été variés. D'autre part, la spectroélectrochimie (UV-Vis) a permis de montrer que le catalyseur se régénère rapidement (k_{cat} = 116 s^{-1}). Des premières informations sur la forme initiale du catalyseur ainsi que des compléments mécanistiques ont été obtenus par spectrométrie de masse. Dans l'acétonitrile, nous avons mis en évidence la présence d'adduits $[LCu^I(CH_3CN)_n]$ (avec n = 1 ; 2). Il a été enfin montré que le TEMPO ne se coordine pas au centre métallique.

À terme, nous obtiendrons des informations structurales et énergétiques sur les intermédiaires réactionnels de ce modèle. Ces résultats seront renforcés par le calcul théorique.

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Induced transparency by coupling of WGM active resonators

L. Ruel[*], **C. Pareige, Y. Dumeige, P. Féron**

Univ Rennes, CNRS, Institut FOTON-UMR 6082, F-22305 Lannion, France
E-mail: louis.ruel@univ-rennes1.fr

Optoelectronic oscillators (OEOs) are an attractive alternative to electrical solutions for the generation of high spectral purity signal at high frequency. Indeed, carrying the microwave signal on an optical carrier offers the opportunity of long storage time, with almost no dependence on signal frequency. For example, classical OEOs are based on kilometre long fiber delays and, in a relative simple setup, their performances exceed the ones of most microwave oscillators. However, the most promising OEOs architectures, in term of performances and integration level, are based on high Q optical resonators ($Q \geq 10^{10}$). Our goal is to realize optical resonators which present a quality factor $Q > 10^{10}$, to overcome the performances of current OEOs. A solution is to use a quantum interference phenomenon named electromagnetically induced transparency (EIT). The destructive interferences create a narrow transmission window (~10 Hz) associated to a strong dispersion[1]. However, this approach require cryogenic cooling and do not correspond to the telecommunications wavelength band. A classical counterpart of EIT can be obtain by coupling two resonators having a common resonant angular frequency ω_0. Such systems are referenced as coupled resonators induced transparency (CRIT)[2]. We illustrate on the figure 1 the coupling of two resonators and the shape of the transmission and the group delay near ω_0 on the second figure. Moreover, the use of active resonators enable the control of the dispersive property of the system, by modifying the gain of the resonators. This way, we are able to control velocity group or the intensity of the transparency[3]. It has been shown that coupled active resonators induced transparency (CARIT) systems can provide 90% transmission and increase the Q factor of the resonators by two order of magnitude.

The first step of our study will be the realization of a CARIT system using Er^{3+} doped micro-spheres as whispering gallery modes (WGM) resonators. These are made in our laboratory using a plasma torch and we obtain spheres presenting high quality factor Q (10^7-10^9). We determine the Q factor of our resonator with a cavity ring-down technique[4]. The CARIT effect let us expect to increase the quality factor up to 10^{11} near 1550 nm.

The second one will be the development of a flattening bench in order to realise disks from our micro-spheres[5].To do so, we will heat the micro-sphere at 300°C and then compress it between two plates of carbon glass. This technique will increase our precision on the diameter of our resonators and allow us to show the potential integration of CARIT systems into OEOs.

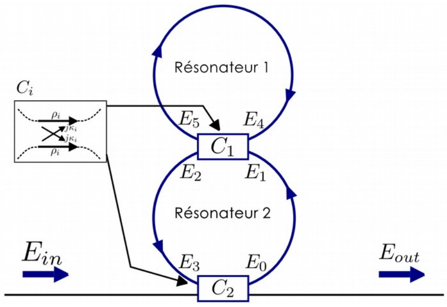

Fig 1. Illustration of two resonators coupled to an access guide. The different couplings are described by 2x2 matrices.

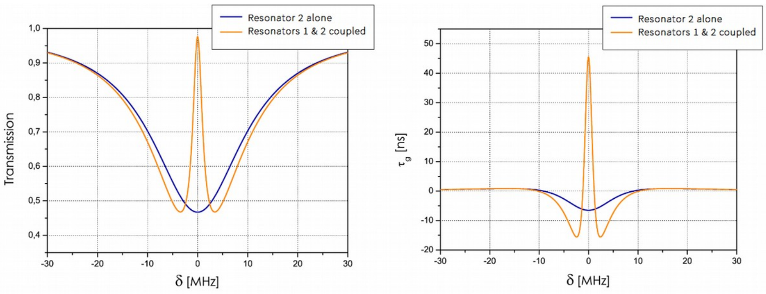

Fig 2. Numerical simulations of the transmission and group delay near ω_0.

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Platform molecules: production and applications, case study succinic acid

A. Salma[1*], R. Abdallah[3], F. Fourcade[1], A. Amrane[1], H. Djelal[1,2]

[1] *Univ Rennes, Ecole Nationale Superieure de Chimie de Rennes, CNRS, ISCR, UMR6226, F-3500 Rennes, France*

[2] *UniLaSalle-Ecole des Métiers de l'Environnement, Campus de Ker Lann, 35 170 Rennes, France*

[3] *Universite Libanaise, EDST, Centre Azm pour la Recherche en Biotechnologie et ses Applications, Rue El Mitein, LBA3B Tripoli, Lebanon*

**e-mail : alaa.salma@ensc-rennes.fr*

Abstract

Platform molecules were defined in a report made by people working for the US Department of Energy. In this report 12 building block chemicals were identified, which can be produced from sugars either by fermentation or synthetically. In a simple view, platform molecule is bio-based or bio-derived chemical with their constituting elements originated wholly form biomass (material of biological origin, excluding carbon fossil sources) and that can be utilized as building blocks for the production of other chemicals. These chemicals can subsequently be converted into a number of high-value bio-based chemicals or materials. Succinic acid (SA) is currently considered a key platform chemical since it is used as precursor for other valuable chemicals. It is a valuable product and has drawn worldwide concerns for its wide application in biodegradable polymers, food, cosmetic, fine chemical, agricultural and pharmaceutical industries. Today succinic acid is mainly produced from fossil resources through maleic acid hydrogenation. It can also be produced through fermentation of sugars by bacterial strains, isolated from rumen such as, *Actinobacillus succinogenes.* The main purpose of this study was the production through biotechnological way (fermentation) of biomass derived building-block chemicals, also called "bio-platform molecules" as a higher value chemicals and materials, for uses in multiple application such as home and personal care products.

Title (in Arial 12-point - Bold)

S. SARR[1],N. GALLAND *[1], J. GRATON*[1]

[1]Laboratoire CEISAM UMR CNRS 6230 Université de Nantes - Faculté des Sciences et des
Techniques 2 rue de la Houssinière, BP 92208 44322 Nantes Cedex 3
**e-mail: Nicolas.Galland@univ-nantes.fr*

The halogen bond is an electrostatic interaction between an electrostatic zone of a halogen atom called a sigma hole and a Lewis base, and a descriptor such as the electrostatic potential makes it possible to predict the strength of such a bond. But recently studies have shown that for **X_3C-I…Z** (with X=F, Cl, Br and I and Z=Cl^- or NH_3) systems this potential does not predict the strength of the halogen bond because this potential decreases when the electronegativity of the X atom increases while the interaction energy decreases with the Afterwards, Clark showed that the electrostatic potential determined at the geometry of the complex but by placing a charge -1 makes it possible to predict the strength of the halogen bond of such systems.
The objectives of our study are to extend these systems to astatine, to test electrophilicity descriptors and finally to determine the effect of spin-orbit coupling on these halogen bonds.

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Acknowledgments (if applicable)

*Abstracts should be submitted in **.doc**, **.docx** or **.pdf** format.*

Development of a Beam Loss Monitor and Transverse Beam Dynamics Studies at ARRONAX C70XP Cyclotron.

A.SENGAR, F.POIRIER, X.Goiziou, F.Haddad

GIP ARRONAX - 1, rue Aronnax - CS 10112 - 44817 SAINT-HERBLAIN Cedex

Sengar@arronax-nantes.fr

The ARRONAX Interest Public Group uses a multi-particle, high energy and high intensity industrial accelerator which has several beam lines used for various purposes. For improvement of operations, ARRONAX has foster and installed robust air-based Beam Loss Monitors (BLMs) outside the beam pipes. BLMs consist of four active detecting plates and are integrated within the experimental physics and industrial control system (EPICS) monitoring and data acquisition system. Each BLM has been tested for the pre-commissioning phase with beams at low intensity (600pA to 6nA on target). Comparative studies and selection of the BLMs has led to their installation at high intensity beam lines. BLMs are now used in beam dynamics studies to investigate transverse characteristics while in regular operation. They support present and future operations extension foreseen at ARRONAX. The results from experimental studies on BLMs at low beam intensity and status of beam dynamics studies at high intensity (A) are presented here.

Keywords: BLM, beam dynamics, EPICS, Gas ionization detector, cyclotron, proton.

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Rayleigh - Taylor instability in a foam film

E. Shabalina[1], **A. Bérut**[1], **and I. Cantat**[1]
[1]Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France .
E-mail: evgenia.shabalina@univ-rennes1.fr

Foam coarsening or shearing induces strong stretching deformation in foam films. A better understanding of the local flows in the films during such transformations is a crucial step to understand the origin of the effective viscosity of the foam.

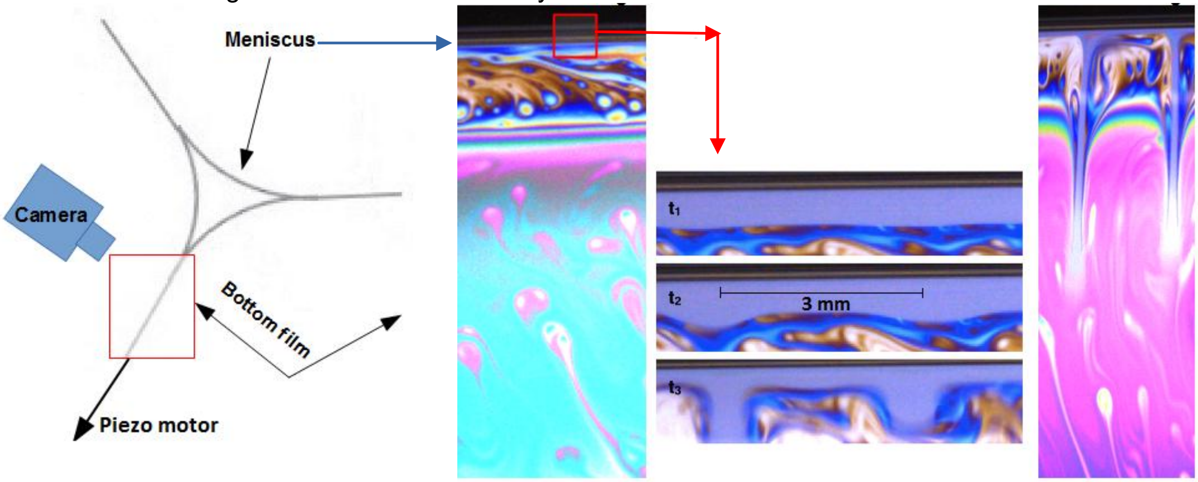

Figure: (from left to right) (a) Set-up, side view. (b) Bottom film before deformation. (c) Zoom in the red rectangle at 3 times during destabilization. Uniform purple: thick film ; bright colors : thin film. (d) Bottom film at a latter time in the non linear digitation regime.

In this aim we built an original set up made of three liquid films connected by an horizontal meniscus. The area of the bottom lateral film area is controlled by a piezo motor. The size of the meniscus is controlled by the steady injection of foaming solution along the lateral frames, and measured optically. A spectral camera is used to observe the film thickness evolution during and after motor motion. From this camera we get 3D information: spatial, temporal and spectral, from which we deduce accurately the film thickness along a vertical line. A color camera provides the full 2D thickness map (see figure), with a qualitative resolution.

When we stretch the bottom film by moving the piezo stage with different velocities (5 - 40 mm/sec) and amplitude (2-10 mm), we observe a thick film extraction rapidly followed by a destabilization of the frontier between the thick and thin parts of the film. The thick film (extracted Frankel's film) is above the thin film (initially present) and the observed instability is an original form of the Rayleigh-Taylor instability, governed by the gravity and the thickness difference which plays the role of the density contrast. We propose a linear model as in [1] to predict the observed wavelength, and found a good agreement with observations.

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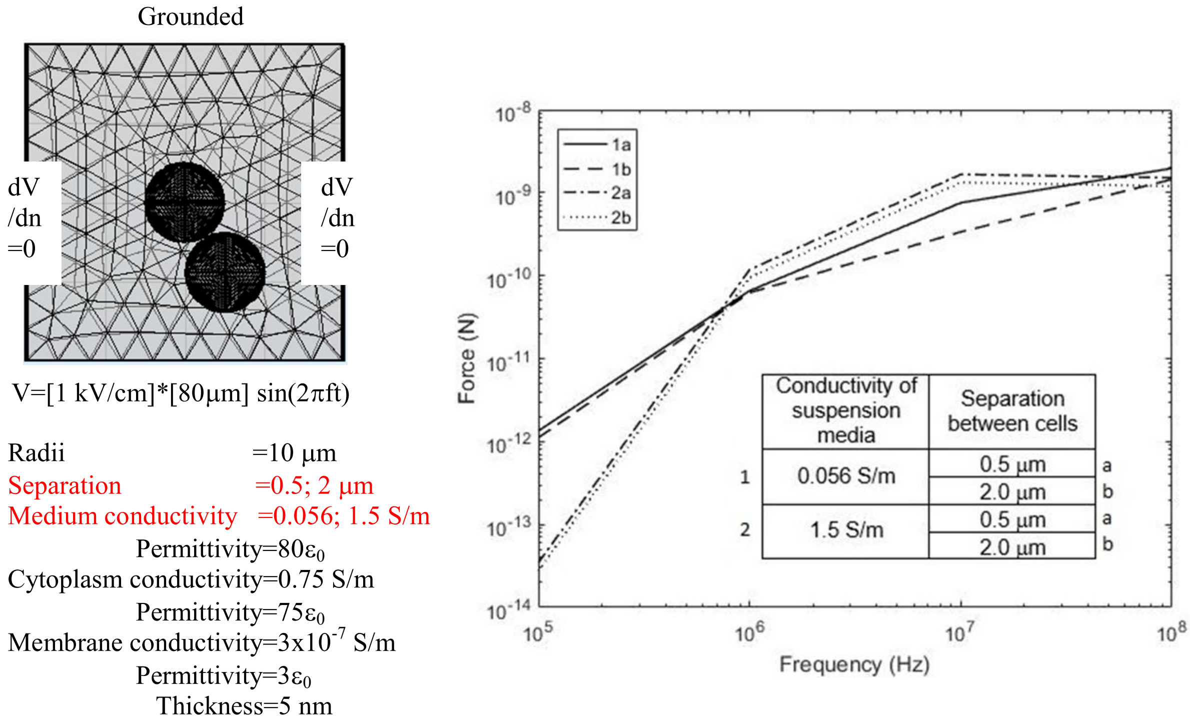
CONTROLLING INTERCELLULAR ELECTRICAL FORCES

D. Shamoon*, **S. Lasquellec, C. Brosseau**

Univ Brest, Lab-STICC, CS 93837, 6 Avenue Le Gorgeu, 29238 Brest Cedex 3, France
**e-mail: (danish.shamoon@univ-brest.fr)*

Biological cells can be considered as polarizable spheres. The polarization of the cells occurs under an externally applied electric field. When these cells are in proximity to each other, the polarization can be affected based on the location of the nearest neighbouring cells. This effectively results in redistributing the interfacial surface charges at the cell membrane leading to change in electrical forces exerted on the cell.

In this work, we analyse the magnitude of total electric force on a simple model of a biological cell in proximity to one identical neighbouring cell under an externally applied electric field with different frequencies. We show that there is orders of magnitude difference in the total force which can be exploited to control intercellular forces based on controlling either the pulse parameters or the conductivity of the suspension media.



Radii =10 μm
Separation =0.5; 2 μm
Medium conductivity =0.056; 1.5 S/m
Permittivity=$80\varepsilon_0$
Cytoplasm conductivity=0.75 S/m
Permittivity=$75\varepsilon_0$
Membrane conductivity=$3\text{x}10^{-7}$ S/m
Permittivity=$3\varepsilon_0$
Thickness=5 nm

	Conductivity of suspension media	Separation between cells	
1	0.056 S/m	0.5 μm	a
		2.0 μm	b
2	1.5 S/m	0.5 μm	a
		2.0 μm	b

Fig.1 3D-FEM for two neighbouring cells with boundary conditions and parameters specified (left); Graph showing orders of magnitude differences in total force on a cell in typical cellular suspensions under an applied AC electric field (right)

Some variations of this work can be found in these references[1,2] and yet the parameter space remains to be explored. There are mainly two situations for the extra cellular conductivity in cell suspensions such that it has either more or less conductivity than the cell. We calculated the force on a cell the cases mentioned in the table that clearly demonstrates up to four orders of magnitude difference as the frequency of the applied AC field is varied. We hope this work can be extended to construct a protocol for cellular assembly and dis-assembly.

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Bi-based hybrid perovskite materials for photovoltaic applications

A. Skorokhod[1*], **N. Mercier**[1]

[1]*MOLTECH-Anjou - UMR 6200 CNR, Université d'Angers, Faculté des Sciences, Bât. K*
2 Boulevard Lavoisier, 49045 Angers,
[*] *alla.skorokhod@univ-angers.fr*

Hybrid organic−inorganic perovskites stand among the most promising photoactive materials because of their excellent physical properties including strong absorption coefficients, high mobilities, and long carrier lifetimes[1-3]. Organic–inorganic lead halide perovskites attracted the attention of many researchers as efficient and low-priced light absorbers. The recently achieved perovskite solar cells has a record efficiency of 23,7%[4]. However, the lead-based perovskites have two major disadvantages as toxicity[5] and low stability, what have raised considerable concerns for their real applications. They are not stable under the influence of such factors as heat, humidity, and light soaking[6]. Therefore, most recent efforts have been focused on the design of novel stable environmentally friendly perovskite materials via substitution of lead[7].

Bismuth-based (Bi-based) hybrid organic−inorganic halides, which show a low toxic effect on the human body[8] and much better stability under ambient atmosphere than lead perovskites[9], are most competitive candidates towards lead-free perovskites for solar cells. Here, we reported a new zero-dimensional (0D) light-absorbing hybrid material of $(AV)_3[BiI_6]_2$ with AV^{2+} a 1,1'-difonctionalized-4,4'-bipyridiniium as organic cation (Fig. 1a). A two kind of the individual metal halide octahedra of BiI_6 represent the inorganic part. Obtained bulk black crystals and thin films (Fig. 1b, c) of $(AV)_3[BiI_6]_2$ show excellent stability in condition of humidity and under direct sunlight, what was proved by X-ray diffraction analysis. As shown in Figure 1e, the absorption spectrum of thin film shows an absorption cut off wavelength of 783 nm, similar to the known lead halide perovskite light-absorbing materials[2]. In the same chemical system, we also synthesized the saturated black thin films (Fig. 1d) from DMSO solution of AVI_2 and BiI_3 in 1:1 molar ratio. The principal peaks of diffractogram of this films are similar to the theoretical diffractogram of analogous compound $(MV)[BiI_3Cl_2]$ (MV = methylviologen)[10], which indicates the formation the one-dimensional (1D) chain based hybrid $(AV)[BiI_5]$.

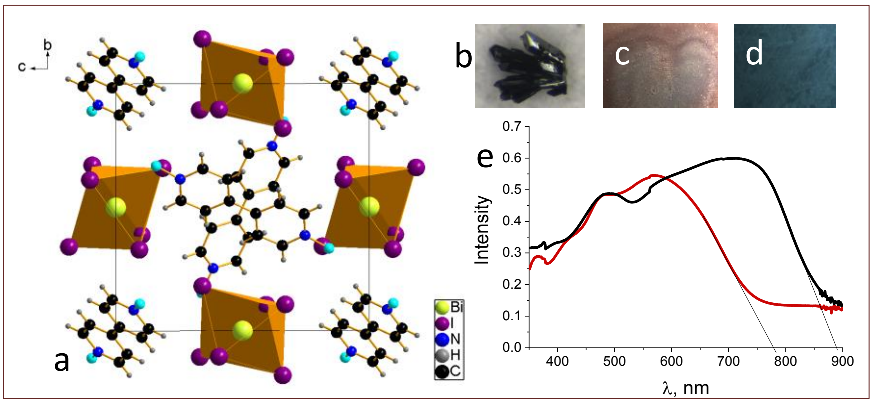

Figure 1. Three-dimensional structure (a), crystal (b) and thin film photographs of $(AV)_3[BiI_6]_2$ (c), UV-visible absorption spectrum (e) of thin film of $(AV)_3[BiI_6]_2$ (red line); photograph (d) and UV-visible absorption spectrum (e) of thin film of AVI_2/BiI_3 (1:1) (black line).

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Diffractive Optical Elements for Illumination and Light Manipulating: Design and Fabrication

Qiang Song
Optics Department, IMT Atlantique, 29238 Brest, France

**e-mail*: qiang.song@imt-atlantique.fr

Diffractive optical element (DOE) has attracted extensive attention in the community of optics owing to their versatility in function, light weight and compactness. In recent decades, with the rapid development on photo-lithography technology, fabricating DOEs has became feasible and economical, thereby leading to a wide utilization DOEs in application, such as wave-front correction, beam shaping , beam splitter, laser material processing , three-dimensional reconstruction , facial recognition , optical network and so on. Our team focus on the field of DOE design and fabrication, especially in illumination application for LED source, light shaping and holographic display for laser source. Here, this work will give an introduction of the DOE's physical principle first, then the DOE design algorithm will be described in Section 2. Fabrication process will be demonstrated in Section 3, and some different functional DOE samples will be presented in Section 4. Conclusion is given in Section 5.

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Optical properties of As-Se and Te-As-Se-based glasses modified by Sb and Ga

J. Szlezak*[1,2], Ya. Shpotyuk[1], C. Boussard-Pledel[2], J. Cebulski[1], B. Bureau[2]

[1]Faculty of Mathematics and Natural Sciences, University of Rzeszow, Rzeszow, Poland
[2]Glass and Ceramic Laboratory, UMR-CNRS 6226, University of Rennes 1, Rennes, France
**e-mail: jakub.szlezak@univ-rennes1.fr*

The state of the art in the modern IR photonic devices permits to say that an applicatory field of chalcogenide glasses (ChG) fabricated by classic melt–quench procedure is authentically largescale due to their exceptional properties in the IR region and relatively low manufacturing cost [1].

Recent progress in this branch of advanced IR optical materials is concentrated, among the others, on enhancement of solubility of rare earth (RE) ions in ChG matrices for the development of effective remote sources of light [2-3]. It was proven, that Ga constituent introduced into chalcogenide glass has positive impact on RE distribution [2-3]. In contrary to affirmative effects of Ga-doping, the eventual possibilities of minimization of negative outcome of Ga-addition (decrease in glass stability) has to be comprehensively studied.

In this work, effect of Sb addition on physical properties of Ga-doped As_2Se_3 and $Te_2As_3Se_5$ alloys within $Ga_x(Sb_yAs_{0.4-y}Se_{0.6})_{100-x}$ system (x = 2, y = 0; x = 2, y = 0.12; x = 5, y = 0.12) and $Ga_xSb_yAs_{30-x-y}Te_{20}Se_{50}$ (x = 2, y = 8; x = 5, y = 8) is examined for further development of efficient matrix hosts for RE ions. The synthesized $Ga_x(Sb_{0.12}As_{0.28}Se_{0.6})_{100-x}$ alloys with 2 and 5 at.% of Ga showed good homogeneity and optical properties. No crystallization processes were observed in Sb-modified glass even in case of 5 at. % of Ga. On the other hand, 5at.% of Ga introduced into TAS matrices led to parasitic bulk crystallization effects, what in general, reflects less ability for an simultaneous modification by Ga and Sb for this system.

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Coating by fine Magnesium-based mineral in dry conditions

M. Tansu[1,2], **J. Duclos**[*2], **T. Bataille**[1], **E. Le Fur**[*1]

[1] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France
[2] Timab Magnésium, R&D department, 55 Boulevard Jules Verger, F- 35800 Dinard, France
*E-mail : eric.le-fur@ensc-rennes.fr ; julie.duclos@roullier.com

Keywords : Magnesium, Dry coating, Ordered mixture.

Wet particle coating has been extensively studied and the industrials applications have indeterminate number of fields. Environmental problems created by the use of solvent in a wet process led researchers and industrials to investigate the dry coating. Contrary to solvent processes, this technique does not favour the mobility of the materials composing the core and the shell of the particles. Thereby, their physical properties become essential. When mixing two different powders in dry conditions, the evolution of the mixture mainly depends on both the physical differences between the two materials and the intensity of the shear and frictional forces. Particle density and size are the main parameters to be considered. Indeed, if the two materials to be mixed have similar parameters, then the mixture will lead to random particles, while the homogeneity will only be dependent on the mixing duration. On the contrary, powders having significantly different properties will give a so-called "ordered mixture". In other terms the small particles go around the big ones. It usually results in a better homogeneous mixture than in the first case.

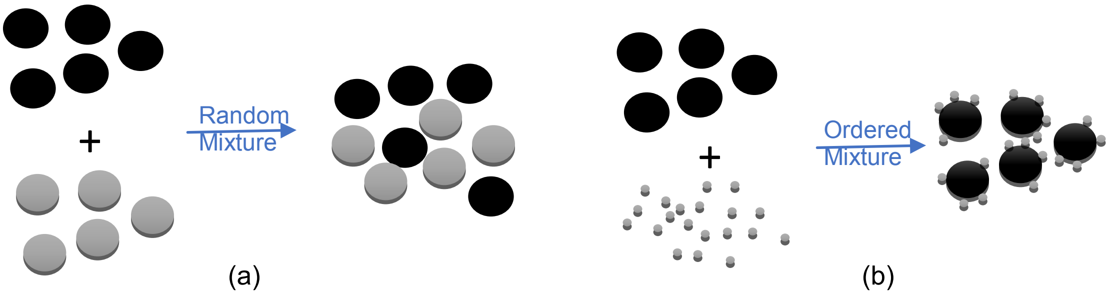

Figure 1 : Processes for (a) random mixture and (b) ordered mixture.

Different ways of magnesium-based mineral coating are under investigation in this work: fluidization, deposit by drying a concentrate liquid on the coarse material, mixing of fine and coarse particles and co-sintering.

The core particles used for the experiments is a reference material with a defined spherical granulometry. They are mixed with smaller particles of variable size for the preparation of ordered mixture. Some techniques like fluidization lead to particles recovery of only 30 % while others show recoveries up to 80 %.

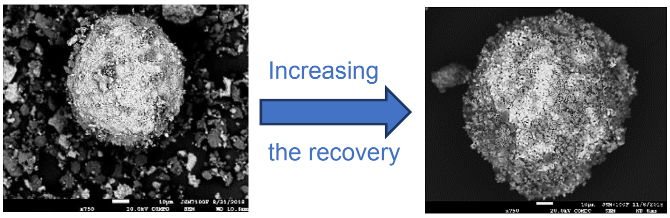

Figure 2 : BEM views of the magnesium-based mineral (dark) recovering the core materials (light).

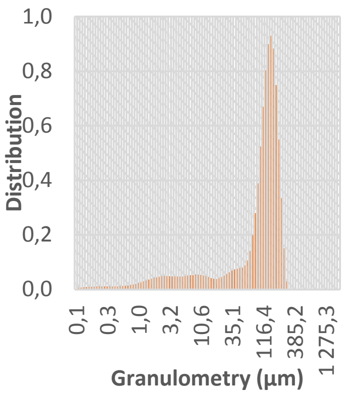

Figure 3: Volume distribution of the core material.

Acknowledgments : A.N.R.T

Stabilisation of water-water emulsions (PEO-dextran) by chitosan

<u>L. TEA</u>[1], F. RENOU[1], T. NICOLAI[1]

[1]Le Mans Université, IMMM UMR-CNRS 6283, Polymères, Colloïdes et Interfaces, 72085 Le Mans, cedex 9, France

Emulsions are formed when to non-miscible liquids are mixed, the most known are oil-in-water emulsions (cosmetic cream) or water-in-oil emulsions (mayonnaise), but it also is possible to make other types of emulsions such waterwater or oil-oil emulsions. To form a water-water emulsion, two aqueous solutions of incompatible polymers are mixed. similarly to every emulsion, water-water emulsions are thermodynamically unstable and tend to phase separate to minimize the contact between the two incompatible polymers. Hence, in order to use these kind of emulsions, in food industry for instance, one has to stabilize them. Unlike oil-water emulsions, the use of surfactant to stabilize water-water emulsions is not possible. Indeed, water-water emulsions present a very low interfacial tension, three orders of magnitude less than oil-water emulsion, and a thick interface of tens of nanometers.

Stabilization of water-water emulsions are well studied in the literature, mainly by geling of the continuous phase, to slow down or even stop droplet motion, or by using particles as interface stabilizer, called Pickering effect. For oil-water emulsions, use of particles is efficient to stabilize the emulsions, but for water-water emulsions, adsorption of particles at the interface doesn't always prevents coalescence and then the phase separation.

In this study, the objective is to stabilize water-water emulsions by polymer. The later should present affinity with both phases to locate at the interface, but should not interact preferentially with one of the two polymers to avoid migration of the stabilizing polymer to one phase. For that purpose, we used a model emulsion made of PEO-dextran. The use of chitosan at low concentrations is efficient to stabilize these emulsions for weeks while the same emulsion without chitosan phase separated within few hours. Since chitosan has a weak acid character, the emulsion stability is thus both pH and ionic strength dependant.

The emulsions structures and kinetics are characterized by confocal microscopy, rheology in order to understand stabilization mechanisms involved..

Alkali organic salt of tetramethylpiperidine N‑oxyl for aqueous organic redox flow battery

S. TOUNSI*[2] , **J. Gaubicher***[2], **D. Pasquier***[1], **P. Poizot***[2],

[1]Institut Français du Pétrole et des Energies Nouvelles (IFPEN), Rond-point de l'échangeur de Solaize
B.P. 3, 69360 Solaize, France,
[2]Institut des Matériaux Jean Rouxel (IMN), UMR CNRS 6502, Université de Nantes, 2 rue de la
Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France
e-mail : sayda.tounsi@cnrs-imn.fr

The urgent need for cleaner energy technologies calls for a radical change in the energy mix to favor renewable energy (+138.5 GW added in 2016 [1]) and environmentally responsible energy storage solutions. Within this background, the development of reliable, efficient, low-polluting and low-cost electrochemical storage systems can be considered as particularly important. Among the various possible technologies, Redox Flow Batteries (RFBs) is believed as suitable devices for large-scale energy storage [2]. Basically, both physico-chemical and electrochemical properties of the selected redox-active species are particularly crucial. Thus their solubility, chemical stability and the resulting output voltage (after assembly) define the energy density, the cyclability and the power density of the system, respectively. Interestingly, the use of organic electroactive species enable access to low cost and possibly greener compounds because composed of naturally abundant elements. Moreover, they offer high structural designability through the well-established principles of organic chemistry and notably access to both n- and p-type electrochemical storage mechanisms [3–5].

As part of our ongoing effort in developing novel Aqueous Organic Redox Flow Batteries (ORFBs), we will present our recent results dealing with the synthesis and characterizations of a novel highly soluble organic derivative used as catholyte and based on the stable tetramethylpiperidine N–oxyl moiety [6,7]. The electrochemical properties of the catholyte will be reported as well as preliminary data obtained in a full flow battery configuration.

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STRAIN RATE SENSITIVITY OF GERMANIUM-SELENIUM GLASSES
Title (in Arial 12-point - Bold)

G Trenvouez[1], C Bernard[2], M. Nivard[1], V. Keryvin[2], J-P Guin[1]

[1]Institut de Physque de Rennes, Université de Rennes 1, Rennes FRANCE
[2]Laboratoire d’Ingénierie des Matériaux de Bretagne, Univeristé de Bretagne Sud, Lorient FRANCE
**e-mail: gwenole.trenvouez@univ-rennes1*

Chalcogenide glasses are widely used in optical applications either as information carrier or as sensors due to their optical transparency in the mid-infrared window (8-15µm), high refractive index and non linearity. Glasses from the GexSe1-x system have been extensively studied over the last decades because some of their physical properties do show an anomalous behaviour (Tg, density, band gap, indentation fracture toughness) at certain specific compositions for instance at x=20% also called the percolation threshold.

In this work we studied the indentation behaviour of GexSe(1-x) (0≤x≤30) under constant strain rate conditions. Instrumented Berkovich micro indentation were performed at different strain rates (from 10^{-3} to 10^{-1} s^{-1}) at ambiante temperature, indentation residual imprints were image by atomic force microscopy. Energies at stake during indentation, strain rate sensitivity (computed from Norton’s law) as well as indentation imprints shape and volumes are discussed as a function of the litterature and glass structure. Experimental results are in good agreement with a similar study based on pure Se glass. From AFM pictures a transition behaviour is identified near the percolation threshold.

Demonstration of an Optical Parametric Oscillator(OPO) in monolithically integrated GaP/Si microdisks

R.S. Urothodi*, C. Pareige, J. Stervinou, T. Rohel, C. Cornet, P. Féron, Y. Léger, Y. Dumeige

Univ Rennes, CNRS, Institut FOTON – UMR 6082, F-22305, Lannion, France
**e-mail: rasool-saleem.urothodi@univ-rennes1.fr*

On-chip photonic communication requires routing different wavelengths and their conversions. Nonlinear devices like OPO are good wavelength converters, but still, their on-chip realization is a difficult task. In recent years, GaP is found to be an alternative nonlinear material for fabricating integrated photonic devices. It indeed features a wide and indirect band-gap at the datacom(~850nm) and telecom(~1550nm) windows[1], high $\chi^{(2)}$ susceptibility in between $LiNbO_3$ and GaAs, broad transmission range from UV to IR and low surface state density in comparison to GaAs. Microscale optical resonators are essential building blocks of this future technology. In particular, microdisk resonators strongly confine the electromagnetic field into whispering gallery modes(WGM). They possess small mode volume, narrow linewidth, and huge power density suitable for miniaturized photonic devices performing nonlinear wavelength conversions. First demonstrations of photonic circuits featuring GaP-based microresonators have recently be published[2].

This thesis will be focussed on demonstrating various 2nd order nonlinear processes in GaP WGM microdisks monolithically integrated on Si. The frequency conversions from the second harmonic generation(SHG) to optical parametric amplification(OPA) and down conversion will be investigated. Phase-matching(PM) condition should be satisfied in the nonlinear process for high conversion efficiencies. In GaP WGM resonators, quasi-phase matching(QPM) can be obtained thanks to the $\bar{4}$-symmetry of the crystal[3]. More than this, natural defects created at the GaP/Si interface during the integration[4] called anti-phase domains(APD) can be used to achieve random QPM and make nonlinear conversion easier[5],[6].

This work will make use of these PM criterions offering a wide tunability for nonlinear wave mixing processes and the studies will be targeted to realize an on-chip broadband tunable OPO. A dedicated setup will be used for conducting optical characterizations. The initial objective of the research activities will be to fabricate dimpled taper fibers using the state-of-the-art technique for coupling the evanescent field efficiently into GaP/Si microdisks. The effect of APD's on the linear optical properties of microdisks for different wavelength regions will then be studied. Thereafter, the research concentrates on experimentally realizing highly efficient SHG and OPO based on $\bar{4}$-QPM and RQPM. For OPO, cw/pulsed excitation will be used for pump-probe experiments. Two wavelength regions are under consideration: λ_{signal} and λ_{idler} around 1550nm for telecom wavelength conversion and photon entanglement(for quantum communication) applications, λ_{pump} close to 850nm and λ_{signal} close to 1550nm for off-chip to on-chip optical data transfer applications. Triple resonance algorithm to predict microdisk geometry for a given OPO process and polarization selection rules will be also developed during the thesis in the theoretical point of view for the complete practical implementation of an on-chip OPO.

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“Click” Dendrimer-Stabilized Nanocatalysts for Hydrogen Evolution upon Ammonia Borane Hydrolysis

Q. Wang[1,2]

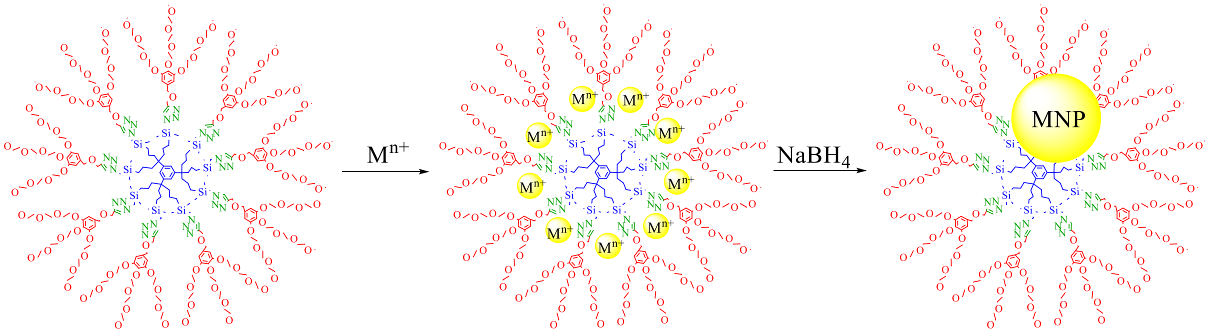
[1]ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence Cedex, France,

[2]Univ. Rennes, CNRS, ISCR – UMR 6226, 35000 Rennes, France

Hydrolysis of ammonia borane (AB) is a very convenient source of H_2, it has attracted much attention because of its high hydrogen content (19.6 wt %), low molecular weight (30.87 g mol^{-1}) and high stability in solution.[1] However, this reaction needs catalyst to become practical under ambient conditions.

Dendrimers have been extensively used as supports and shown to be highly efficient in catalysis, including for the encapsulation or stabilization of transition-metal NP catalysts.[2]

Here, “click” dendrimer **1** contains 27 triethylene glycol terminal groups and 9 1,2,3-triazole ligands was synthesized and used for stabilize late transition-metal nanoparticles (NPs). he noble-metal NPs are as expected much more efficient catalysts than the first-raw transition-metal NPs.



dendrimer **1**   M = Co, Ni, Ru, Rh,Pt   MNP = Metal nanoparticle

Scheme 1. Synthesis of the MNPs/**1**.

For cataylze the hydrolysis of AB, the noble-metal NPs are as expected much more efficient catalysts than the first-raw transition-metal NPs. NaOH was shown to boost the reaction rate, except for the PtNPs/**1**. A TOF of up to 611 mol_{H2} $mol_{catalyst}^{-1}min^{-1}$ for RhNPs/**1** at 20 °C is obtained, which is one of the best results among the literature.

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DIAGNOSTIC ON NONLINEAR OPTICAL RESPONSE OF SOME SLECTED SUPRAMOLECULAR SYSTEMS

Karolina Waszkowska[1,*], **and Bouchta Sahraoui**[1]
[1] *Laboratory MOLTECH-Anjou, CNRS UMR 6200, University of Angers, 2 bd Lavoisier,*
49045 Angers Cedex, France
**e-mail: karolina.waszkowska@etud.univ-angers.fr*

This work presents diagnostic on the nonlinear optical properties of organic metallo-supramolecular systems such as triple helicates containing two metal cation resulting of self-assembly process [1]. Samples containing four different metal cations were tested as their dependence on the studied nonlinear optical properties (fig. 1a). Furthermore supramolecular complexes containing fullerenes with porphyrin derivatives were investigated [2]. Nonlinear optical effects were studied on thin films deposited by two different methods: spin coating and physical vapour deposition. The second and third harmonic generation responses were investigated by using Maker fringe technique in transmission manner [3]. The experimental results (fig. 1b) allowed to determine the second-order hyperpolarizability and the third-order susceptibility by using theoretical models. Otherwise, Z-scan technique allowed to obtain the imaginary part of third-order susceptibility and also the nonlinear absorption coefficient. It was found that investigated nonlinear optical properties permit to for use studied supramolecular systems in novel photonic devices.

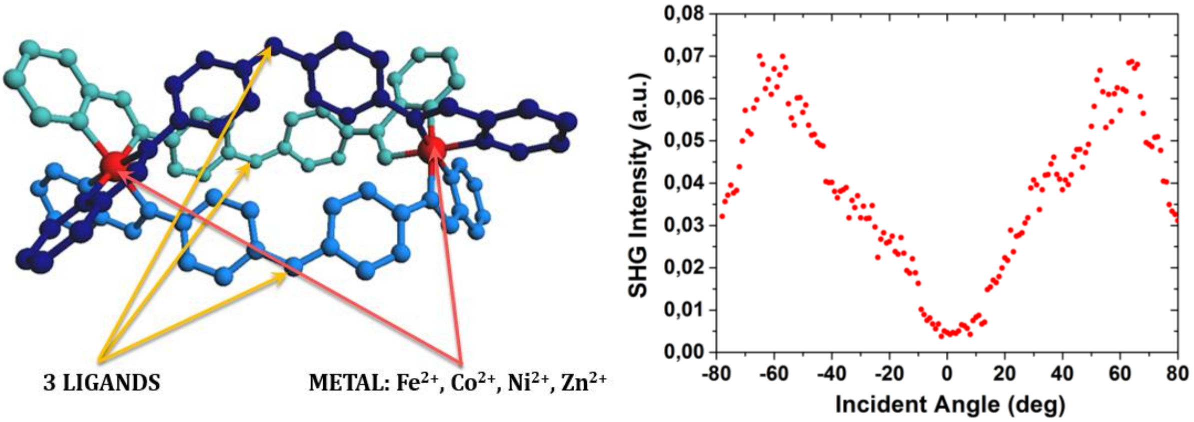

Figure 1: a) Supramolecular triple-helicates; b) Typical second harmonic generation signal of diagnosed supramolecular systems.

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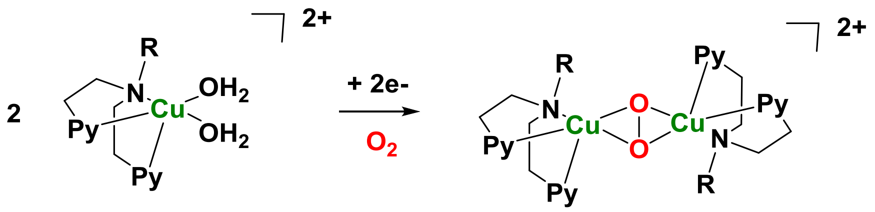
Low temperature spectroelectrochemistry of a peroxo dicopper complex derivated from a RPY2-type ligand

L. Wojcik *[1], N. Le Poul[1], J. Simaan[2], M. Réglier[2]

[1] CEMCA, UMR CNRS 6521, Université de Bretagne Occidentale, 6 avenue Le Gorgeu, 29238 Brest Cedex 3 France , [2]ISM2 , UMR 7313, Aix-Marseille, CNRS, Centrale Marseille, 13397 Marseille, France.

e-mail: laurianne.wojcik@univ-brest.fr

Copper centers play a key role in chemical oxidation reactions involving molecular oxygen. In biological processes, copper enzymes are capable of selectively oxidizing substrates through the formation of transient Cu_n:O_2 species generated by the reaction of copper(I) and O_2. Over decades, several types of these copper-dioxygen adducts such as superoxide, peroxide and oxide have been identified in metalloproteins[1] and in their bioinorganic model Cu complexes.[2] While a good number of X-ray structures, spectroscopic UV and Raman data of copper-dioxygen complexes have been reported, few data are available concerning redox potential and electron-transfer properties.[3-5] Here, we report our investigations about the formation of a peroxo dicopper complex derivated from RPY2-type ligand[6] by using cryo-electrochemistry and cryo-spectroelectrochemistry.



R=Allyl; Py= Pyridyl

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Mid-infrared Emission Properties of Dy^{3+} doped $CaLa_2S_4$ Powders

R.YE[1, 2], O. Merdrignac-Conanec[1], X. Zhang[1]

[1]Univ Rennes, CNRS, ISCR (Insitut des Sciences Chimiques de Rennes)–UMR6226, Rennes, France,
[2]INSA de Rennes, France
**e-mail: (renguang.ye@univ-rennes1.fr)*

Rare earth doped mid-infrared (MIR) fluorescent sources have been widely investigated due to their various potential applications in the fields of communication, chemical detecting, medical surgery and so forth [1]. Calcium lanthanum sulfide ($CaLa_2S_4$) is one of the members of the family of ternary sulfides with the general formula AB_2S_4 (where A is a divalent metal cation and B is a trivalent metal cation). Therefore, rare earth ions can be easily doped into the lanthanide site of the crystalline matrix. Moreover, $CaLa_2S_4$ exhibits a low phonon energy of 285 cm^{-1}, which is promising for low multi-phonon quenching of the MIR rare earth transitions. Here, $CaLa_2S_4:Dy^{3+}$ powders are prepared by combustion method and post-heat treatment under H_2S [2]. Photoluminescence (PL) spectra indicated that MIR emission was obtained in cubic phase $CaLa_2S_4:Dy^{3+}$ powders for the first time. Under optical pumping at 808 nm, $CaLa_2S_4:Dy^{3+}$ powders exhibited a broad MIR emission centered at 2.95 μm ($^6H_{13/2} \rightarrow {}^6H_{15/2}$) with a bandwidth of 290 nm at full width half maximum. The decay lifetime of the $^6H_{13/2}$ level was measured to be 3.18 ms. To the best of our knowledge, it is the first investigation on MIR fluorescent performance of $CaLa_2S_4:Dy^{3+}$ powders, which may find various applications in many fields.

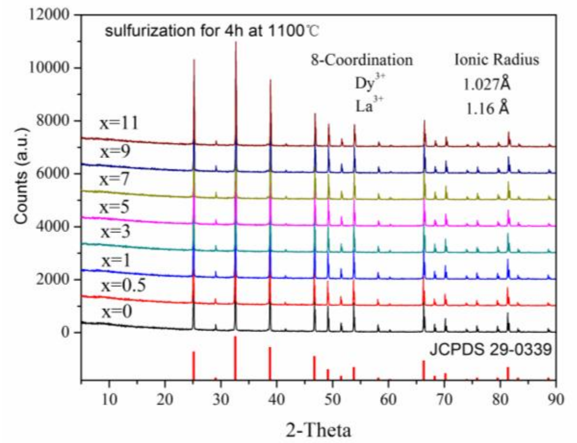

Figure 1. XRD patterns of $CaLa_2S_4$:*x*mol%Dy^{3+} samples sulfurized t 1100°C

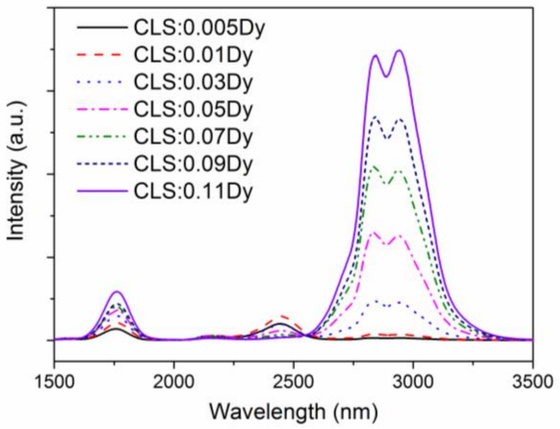

Figure 2. Emission spectra of *x*mol%Dy^{3+} doped $CaLa_2S_4$ powders pumped at 808 nm

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