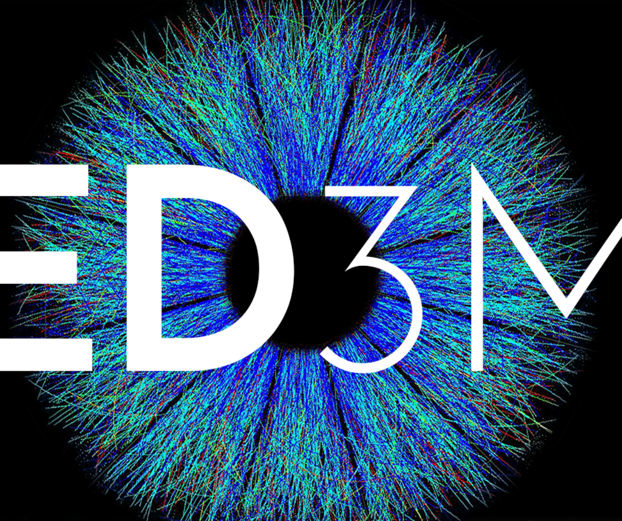

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AU CŒUR DE LA MATIÈRE

27 Juin 2019
Nantes

Conférence plénière

What's the Matter?

par **Dr. Yann Pellegrin** (CEISAM, Nantes)

Renseignements et inscriptions
jed3m2019nantes.sciencesconf.org

UNIVERSITE BRETAGNE LOIRE / MATIERE MOLECULES ET MATERIAUX

Journée de l'École Doctorale "Matière, Molécules et Matériaux"
Laboratoire Subatech – 4 Rue Alfred Kastler, 44307 Nantes

Subatech · IMT Atlantique Bretagne-Pays de la Loire École Mines-Télécom · Université de Nantes · université angers · Le Mans Université · Université de Rennes 1 · UBO Université de Bretagne Occidentale · INSA Institut National des Sciences Appliquées Rennes · Ecole Nationale Supérieure de Chimie de Rennes

Bienvenue !
Welcome!

Nous sommes ravis de vous accueillir au laboratoire Subatech pour cette quatrième édition de la Journée de l'École Doctorale Matière, Molécules et Matériaux ! Autour du thème *Au cœur de la matière*, ce sont 36 présentations orales en sessions parallèles et 41 posters que vous pourrez découvrir tout au long de la journée, à la suite de la conférence en session plénière “What's the Matter?” donnée par le Dr. Yann Pellegrin (laboratoire CEISAM, Nantes).

L'enveloppe qui vous a été fournie contient, en plus du livret que vous avez entre les mains, un bloc-notes, un stylo, ainsi que le ticket repas qu'il vous faudra présenter à la caisse du restaurant ce midi (voir la page 13 à ce sujet). L'ensemble du comité local d'organisation, dont les membres sont identifiables par un badge distinct, se tient à votre disposition en cas de besoin et vous souhaite une excellente journée !

We are pleased to welcome you at the Subatech laboratory for the fourth edition of the Matter, Molecules and Materials Doctoral School Day! Around the theme At the heart of matter*, you could discover 36 oral presentations in parallel sessions as well as 41 posters all day long, following the plenary conference “What's the Matter?” given by Dr. Yann Pellegrin (CEISAM laboratory, Nantes).*

The envelope you were given contains, besides the book you hold in your hands, a notepad, a pen, as well as the meal ticket you will have to show at the restaurant checkout this noon (see page 13 in this regard). The entire local organising committee, whose members can be identified by a distinct badge, is at your disposal if need be and wish you a wonderful day!

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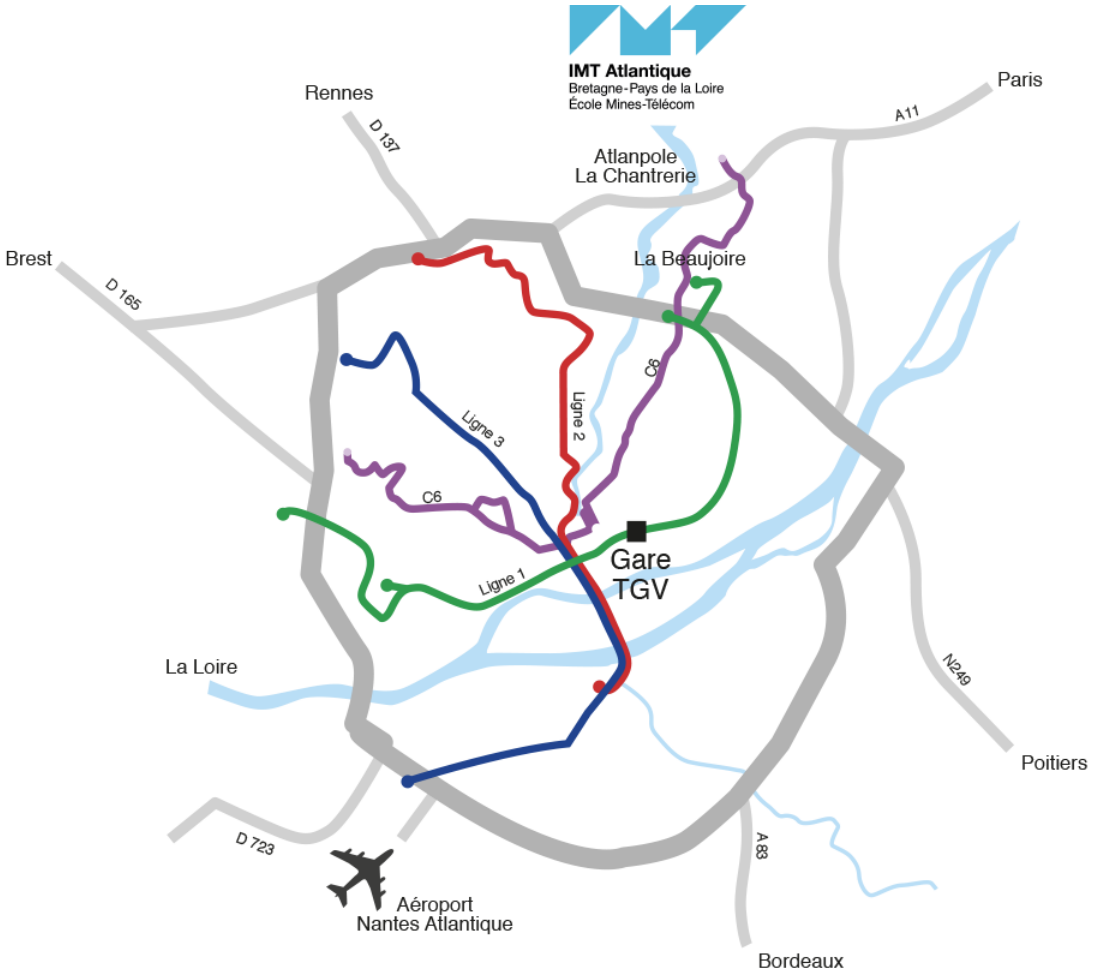
Atteindre Subatech
Getting to Subatech



Le laboratoire Subatech est hébergé à l'IMT Atlantique au sein du campus de La Chantrerie, au nord de Nantes (4 Rue Alfred Kastler, 44307 Nantes). Pour l'atteindre, plusieurs possibilités s'offrent à vous :

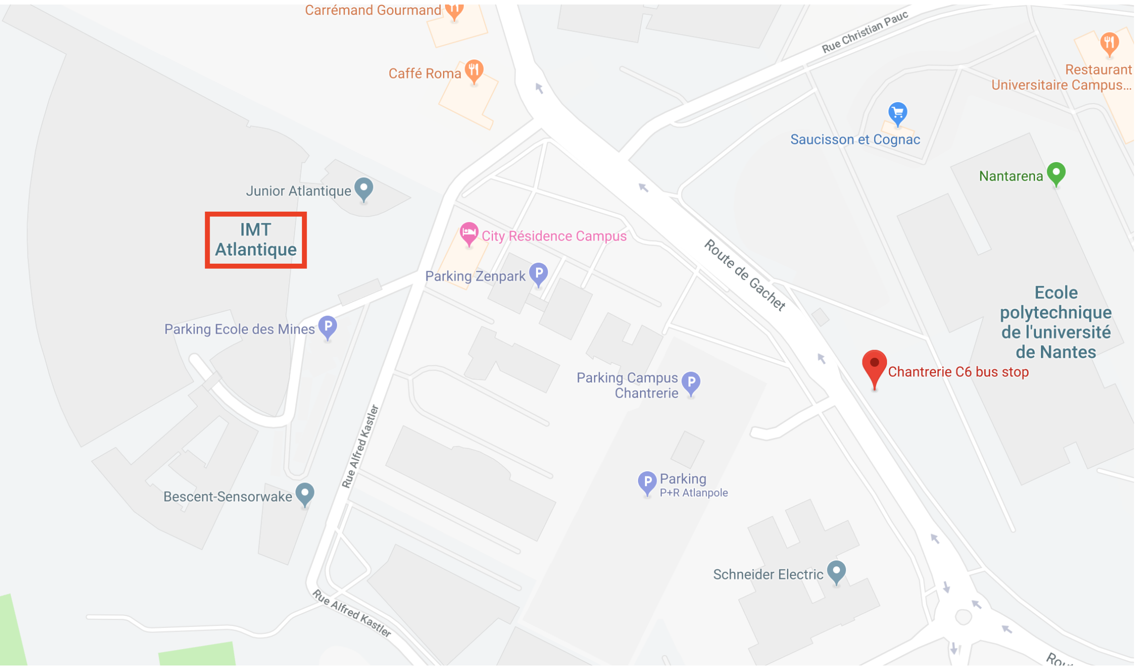
- par train, depuis la Gare SNCF de Nantes prenez la **ligne 1 de tramway à la station Gare–Jardin des Plantes vers Beaujoire** (attention, cette ligne a deux terminus, Beaujoire et Ranzay) et descendez à son terminus (Beaujoire). Prenez ensuite le **bus C6 vers Chantrerie–Grandes Écoles** ou le **bus 75 vers Charbonneau** et descendez à Chantrerie–Grandes Écoles. Il faut compter environ

40 minutes de trajet. Le site internet des transports nantais vous permet de connaître les horaires et itinéraires possibles ;

- par voiture, sur l'autoroute A11 prenez la **sortie 23 en direction de Nantes**, ou la **sortie 24 en direction de Paris**.

The Subatech laboratory is housed at IMT Atlantique in La Chantrerie campus to the north of Nantes (4 Rue Alfred Kastler, 44307 Nantes). To get there you have several options:

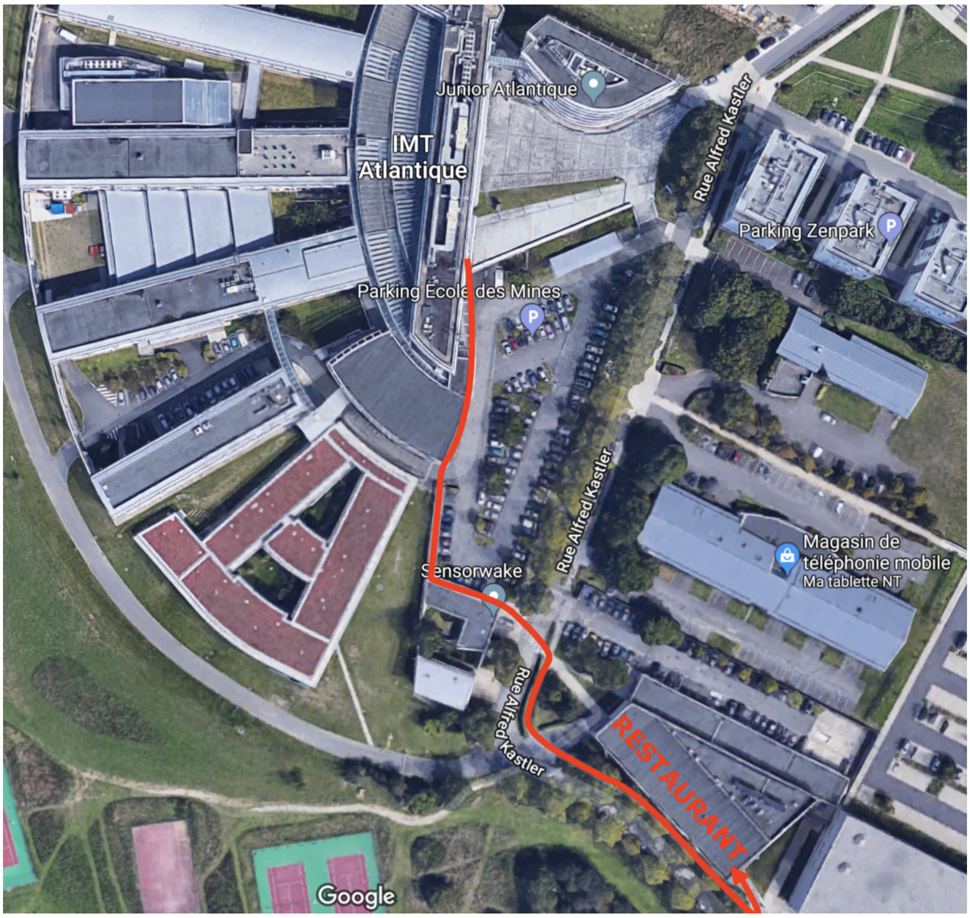
- *by train, from the Nantes SNCF railway station take the* ***tramway line 1 at the Gare–Jardin des Plantes station to Beaujoire*** *(be careful, this line has two termini, Beaujoire and Ranzay) and get off at its terminus (Beaujoire). Then take* ***bus C6 to Chantrerie–Grandes Écoles*** *or* ***bus 75 to Charbonneau*** *and get off at Chantrerie–Grandes Écoles. You need to allow about 40 minutes to travel. The Nantes public transport website allows you to determine the possible hours and routes,*
- *by car, on motorway A11 take* ***exit 23 in the direction of Nantes*** *or* ***exit 24 in the direction of Paris****.*



Une fois arrivé sur le campus de La Chantrerie par les transports en commun, marchez 5 minutes vers l'imposant bâtiment vitré de l'IMT Atlantique.

Once arrived in La Chantrerie campus by public transport, walk 5 minutes towards the impressive, glazed building of IMT Atlantique.

Atteindre le restaurant
Getting to the restaurant



Une fois que votre session parallèle du matin est terminée, vous pouvez directement vous diriger vers le restaurant **sans oublier votre ticket repas**. Rendez-vous ensuite à 14:00 dans le Forum. Bon appétit !

Once your morning parallel session is over, you can go straight to the restaurant ***without forgetting your meal ticket****. Then, let's reconvene at 2:00 p.m. in the Forum. Bon appétit!*

Programme

Timetable

jeudi 27 juin 2019

›9:00 (30min)
Café d'accueil
› Forum

›9:30 (1h)
What's the matter?
Dr. Yann Pellegrin (CEISAM, Nantes)
› Amphi CHARPAK

›10:30 (45min)
Pause / Session Poster

›11:15 (1h30)
Présentation
› Amphi BESSE

›11:15 (1h30)
Présentation
› Amphi CHARPAK

›11:15 (1h30)
Présentation
› Amphi PASCAL

›12:45 (1h15)
Déjeuner
› Restaurant

›14:00 (45min)
Pause / Session Poster

›14:45 (1h30)
Présentation
› Amphi BESSE

›14:45 (1h30)
Présentation
› Amphi CHARPAK

›14:45 (1h30)
Présentation
› Amphi PASCAL

›16:15 (15min)
Mot du directeur de l'ED
› Amphi CHARPAK

Amphithéâtre Charpak
Charpak Amphitheatre

What's the Matter? – Plenary conference

9:30

Pellegrin Y.[1]
[1]CEISAM, UMR 6230, Université de Nantes, France

"Why something rather than nothing?" ask the philosophers.

But first and foremost, can we easily define "something"? One can answer that question today, using the ground-breaking discoveries of the XXth and XXIth centuries where experimental work has unquestionably shown what the matter is made of. But before that, men and women only had the power of their own imagination, coupled to their extraordinary talent for deduction, to answer this troublesome question. In this presentation we embark for a travel in time, back to ancient Greece, and analyze with the eye of a modern chemist the enlightening insights of the founding fathers of chemistry.

11:15

Ion beam monitoring using bremsstrahlung X-rays

Ralite F.[1], Koumeir C.[2], Servagent N.[1], Métivier V.[1]
[1] SUBATECH, Université de Nantes, IMT Atlantique, CNRS/IN2P3, La Chantrerie, 4 rue A. Kastler, BP 20722, 44307 Nantes, France,
[2]GIP ARRONAX, 1 rue Arronax, Saint-Herblain, France

A non-invasive method to monitor online proton beams used in radiobiology experiments is presented. The high spatial and dose accuracies required in this field needs to develop beam monitoring tools measuring information directly from the irradiated medium [1]. For that purpose, the feasibility to use the bremsstrahlung X-rays coming from a PMMA target, as a biological medium surrogate, was investigating in this work.
The experimental set-up irradiated a PMMA target with proton beams in the energy range of 17MeV/u to 50MeV, delivered by the cyclotron ARRONAX [2]. The detection of the bremsstrahlung X-rays was performed by a silicon drift detector in regards to the irradiated medium surface. A model based of the theoretical bremsstrahlung cross sections [3] was developed to compare the experiment data to simulations. The differential cross sections were previously measured on carbon target in order to valid the model on a single element target and to compare the results to data available in the literature [4].
Cross sections were in the range of 10 mbarns.keV^{-1} to 1000 mbarn.keV^{-1}. A significate agreement was found with the model and the literature. Moreover, simulations fitted the bremsstrahlung spectra of the PMMA target confirming the significate sensibility of the method (104 X-rays/nC detected) and the validation of the ion bremsstrahlung model. According to the set-up used, proton beam energy can be monitored with the bremsstrahlung X-rays because of the spectrum hardening, explained by the variations of the bremsstrahlung cross sections. The PMMA thickness can also be monitored until a thickness limit where the bremsstrahlung yield saturates. The PMMA thickness limit and the bremsstrahlung yield increased with the proton beam energy. The PMMA thicknesses of bremsstrahlung yield saturation are respectively 0.15cm, 0.5cm, 0.8cm and >1cm for 16.9MeV/u, 30.1MeV, 39.3MeV and 49.6MeV. For PMMA thicknesses up to 3000µm, the bremsstrahlung yields were respectively 20636±1450 X-rays/nC, 23123±1450 X-rays/nC and 23738±1670 X-rays/nC for beams of 30.1MeV, 39.3MeV and 49.6MeV, which also confirming the feasibility to monitor the proton beam energy.
The method described is only valid for the set-up used because of the detector efficiency and the X-ray attenuation. A study with other X-rays detectors is required to improve the set-up. Fundamental studies are also expected to link the bremsstrahlung signal to the deposited dose in the biological medium, in order to apply the method to dosimetry and medical applications.

[1] L. Schwob et al, New beam monitoring tool for radiobiology experiments at the cyclotron Arronax, Radiation Protection Dosimetry, 166(1-4), 257-60, (2015)
[2] F. Haddad et al. Arronax, a High Energy and High Intensity Cyclotron for Nuclear Medicine, Eur. J. Nucl. Med. Mol. Imaging, 35, 1377-1387, (2008)
[3] K. Ishii et al, Continuous X-rays produced in light-ion-atom collisions, Radiation Physics and Chemistry, 75, 1135-1163, (2006)
[4] K. Ishii et al, Theoretical detection limit of PIXE analysis using 20MeV proton beams, Nucl. Instr. and Meth. In Phys. Res. B, 417, 37-40, (2018)

Electrochemical stability of coated current collectors for lithium-ion batteries in high voltage region

11:30

Bizot C.[1,2], Blin M.-A.[1], Guichard P.[1], Soudan P.[2], Lestriez B.[2], Gaubicher J.[2] and Poizot P.[2]

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[2]Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France

Confidential abstract.

11:45

Bottomonium production in hadronic collisions at LHC with ALICE

Damas F.[1,2]

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Kastler, BP 20722, 44307 Nantes, France,
[2]IRFU (CEA)

Under extreme conditions of temperature and energy density, nuclear matter passes through a phase where partons are free to propagate, the Quark-Gluon plasma (QGP). This state of matter is experimentally created in ultra-relativistic heavy-ion collisions at the LHC, the world's largest accelerator. A Large Ion Collider Experiment (ALICE) detector is designed to exploit the unique physics potential of hadronic collisions at LHC energies.

Quarkonia, bound states of heavy quarks, are ideal particles to probe the QGP properties. Their measurement makes it possible to estimate the initial temperature of the medium. In this presentation, a study of the bottomonium production in proton-proton and nucleus-nucleus collisions at LHC is reported. The Υ(nS) states are reconstructed *via* their dimuon decay channel, muons detected by the ALICE muon spectrometer. The different steps of the analysis procedure are detailed and first results are shown.

Study of the degradation process of glass ionomer cements by analysis of speckle field dynamics

12:00

El Cheikh A.[1,2], Pellen F.[2], Le Jeune B.[2], Le Brun G.[2] and Abboud M.[1]

[1]Physics department,UR TVA, Faculty of science, Saint Joseph University, B.P. 11-514 Riad EL Solh, Beirut 1107 2050; Lebanon,

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

Generally, quality assessment of a restorative dental material is based on several criteria: the ability of the material to withstand potential degradation, its durability, the stress it exerts on the residual dental structures, its surface wear resistance, its fracture resistance, etc. All these important factors must be taken into account and tested when developing a new dental material. Glass ionomer cements (GIC) possess unique, including adhesion to tooth structure, bioactivity and fluoride release. The aim of this study is to evaluate by analyzing the dynamics of the polarized speckle field how GIC samples, prepared according to two different methods and conserved in water at 35°C, deteriorate. Speckle optical results are compared to rheological one. Two types of samples are prepared. The first type consists of GIC Chemfil®Rock taken alone while the second type comprises GIC Chemfil®Rock and nano-ceramic Ceram.x SphereTEC one prepared according the sandwich technique. Both kinds are handled according to EN ISO 9917-1:2007 and immersed in distilled water at 35°C. In our experiments, speckle image are acquired by illuminating the samples with a He-Ne laser (632,8 nm) and recorded using a CMOS camera. Different light configurations are considered: once with a linear polarized beam and once with a circular polarized one. We analyze the series of speckle images and we calculate speckle parameters (spatial contrast, speckle grain size, degree of light polarization as well as temporal correlation coefficient) to evaluate the effects of the GIC degradation process. Finally rheological measurements are performed to monitor the variation of the density for GIC Chemfil®Rock and GIC Chemfil®Rock and nano-ceramic Ceram.x SphereTEC one as a function of water immersion time. Correlations between these measurements and speckle optical results show that speckle can potentially be used in order to evaluate the degradation process of GIC. Exploitation of this optical phenomenon could allow developing low-cost, non-invasive and reliable investigation tools in dentistry.

12:15

Improved CGSe thin film for tandem application

Rivalland A.[1], Tsoulka P.[1], Dubois S.[2], Arzel L.[1] and Barreau N.[1]
[1]IMN-CNRS, Université de Nantes,
[2]CEA-INES, LHMJ

To surpass 30% conversion efficiency, tandem solar cells based on crystalline silicon (c-Si) sub-cells seem to be one of the most promising architectures regarding the theoretical predictions. Furthermore a monolithic two-terminal approach using wide bandgap thin films as top cell does not require a significant modification of the solar modules fabrication. $CuIn_{1-x}Ga_xSe_2$ (CIGSe) absorber layer is a promising candidate thanks to its high efficiency (23% for $x = 0.3$, single junction). Additionally, CIGSe permits to tune the bandgap energy from 1.04 ($x = 0$) to 1.68 eV ($x = 1$). Indium-free $CuGaSe_2$ (CGSe) can be used as top cell absorber in a multi-junction device. Nevertheless, the current conversion efficiency of CGSe solar cells is still low ($\eta = 11.9\%$ [1]). The CGSe growth procedure needs to be adapted in order to use this material in a tandem device with c-Si.
We have chosen an alternative CuPRO process [2] for the growth of the CGSe absorber layer on molybdenum. Our preliminary results show that an addition of two annealing steps under Selenium during a CuPRO co-evaporation process improves the performance of the single junction CGSe cell. Considering that the diffusion rate of gallium is low, these additional steps (called “relaxation steps”) would allow a better crystallization and a lower inhomogeneity throughout the absorber layer. This point has been demonstrated by SEM images, EDS analyses and RAMAN measurements.
Furthermore, electrical measurements allow to conclude that the relaxation steps reduce interface recombination rate and increase carrier diffusion length. This induces an increase of J_{SC} and V_{OC} and therefore in efficiency. Indeed for single junction CGSe cells, the conversion efficiency was increased by $2\%_{abs}$ via this original and optimized process.

[1] F. Larsson et al., “Record 1.0 V open-circuit voltage in wide band gap chalcopyrite solar cells,” Prog. Photovoltaics Res. Appl. vol. 25, no. 9, pp. 755–763, 2017.
[2] J. Kessler, C. Chityuttakan, J. Lu, J. Schöldström, and L. Stolt, “CIGS thin film grown with a Cu-poorrichpoor sequence: growth model and structural considerations,” Prog. Photovolt. Res. Appl., vol. 11, pp. 319–331, 2003.

Influence of glass composition on vapor hydration of nuclear waste glasses 12:30

Narayanasamy S.[1], Jollivet P.[1], Godon N.[1], Angeli F.[1] and Abdelouas A.[2]
[1]CEA Marcoule, DEN, MAR, DE2D, SEVT/LCLT, bât 208, BP17171, 30207 Bagnols sur Cèze cedex, France,
[2]SUBATECH, Université de Nantes, IMT Atlantique, CNRS/IN2P3, La Chantrerie, 4 rue A. Kastler, BP 20722, 44307 Nantes, France

In the context of confinement of high-level activity radioactive waste in a vitreous matrix, the behaviour of glass under exposure to vapor phase was investigated. In this framework, 6 glasses [three inactive complex Mg-borosilicate glasses (>20 oxides) and three simplified (Na/Mg-Na/Ca-Na)-alumino-borosilicate glasses (4 to 5 oxides)] were altered in vapor phase (50°C and 95 percent relative humidity) for 180 days and 557 days. The glass response is strongly composition dependent. The significant effect of glass stoichiometry, especially the Al_2O_3/MgO molar ratio, was highlighted by this result. A higher concentration of MgO than Al_2O_3 in two of the glasses resulted in a 10-20 times faster alteration than the other two glasses that contained a lower concentration of MgO than Al_2O_3. In the former case, the alteration rate seemed to be driven by the extensive precipitation of Mg-smectites. These phases precipitation also seemed to affect the morphology of the altered layer. Network-hydrolysis seemed to be the rate-limiting vapor hydration mechanism of the four more durable glasses until 180 days.

14:45

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

Sengar A.[1] and Poirier F.[2]
[1]SUBATECH, Université de Nantes, IMT Atlantique, CNRS/IN2P3, La Chantrerie, 4 rue A. Kastler, BP 20722, 44307 Nantes, France,
[2]GIP ARRONAX, 1 rue Arronax, Saint-Herblain, France

The ARRONAX Interest Public Group uses a multi-particle, high energy and high intensity industrial accelerator which has several beamlines used for various purposes. For improvement of operations, ARRONAX has fostered 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 (600 pA to 6 nA 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 (µA) are presented here.

[1] F. Haddad, L. Ferrer, A. Guertin, T. Carlier, N. Michel, J. Barbet, J. F. Chatal, Arronax, “A high-energy and high-intensity cyclotron for nuclear medicine”. Eur. J. Nucl. Med. Mol. Imaging. 2008, 35, 1377-1387.
[2] F. Poirier et al, “C70 Arronax and beam line status”, IPAC11-WEPS069, 2011.
[3] F. Poirier et al, “Studies and Upgrades on the C70 Cyclotron Arronax”, Proc. 21st Conf. on Cyclotrons and their Applications, CYC2016-TUD02, (Sept. 2016).
[4] D. Vandeplassche et al, “Extraction simulation for the IBA C70 cyclotron”, CYC-2007.
[5] X. Li, “Study of beam losses and monitor for the A1 beamline of the cyclotron Arronax”, master thesis-2014, internal documents Arronax

Fourier Transform incoherent broad-band cavity enhanced absorption spectroscopy of astrophysical anions

15:00

Bejjani R.[1] and Benidar A.[1]

[1]Institut de physique de Rennes, Département de physique moléculaire

The molecular diversity of cold interstellar space has been recently enriched with the detection of molecular anions - all linear carbon chains. Usually by far less abundant than neutrals, anions could play a significant role in the chemistry of molecular clouds.

Our ultimate goal will be to spectroscopically characterize these ionic species. In order to achieve this goal, we have to overcome two difficulties, the low concentration of the production of specific targeted ions and sensitively measure and obtain their spectroscopic signature. An instrument is being developed to tackle these challenges.

This instrument is based on using a planar supersonic flow and an optimized ionization method for the production of targeted species. The produced species will be characterized by Cavity Enhanced Absorption Spectroscopy to record the spectra of carbon chain anions. The spectral data obtained, could then be used to perform an astronomical survey of these species.

15:15

Production of a bio-based chemical, bio-succinic acid, using native strain of Actinobacillus succinogenes and optimization efforts

Salma A.[1], Abdallah R.[2], Fourcade F.[1], Amrane A.[1] and Djelal H.[3]
[1]Univ Rennes, Ecole Nationale Superieure de Chimie de Rennes, CNRS, ISCR, UMR6226, F-3500 Rennes, France,
[2]Universite Libanaise, EDST, Centre Azm pour la Recherche en Biotechnologie et ses Applications, Rue El Mitein, LBA3B Tripoli, Lebanon,
[3]UniLaSalle-Ecole des Métiers de l'Environnement, Campus de Ker Lann, 35 170 Rennes, France

Succinic acid is a precursor of many important, large-volume industrial chemicals and consumer products and was ranked by United State Department of Energy (US DOE) as one of 12 top value added chemicals list. Before the development of fermentation processes for its production, succinic acid was manufactured by catalytic hydrogenation of maleic anhydride, which is a fossil-based chemical. However, due to the increase of oil prices, climate change as well as dwindling of oil supplies, its production from renewable feedstocks started to gain attention. Succinic acid lends itself to biological production because it is part of every organism's central metabolism. Many studies demonstrated the feasibility of succinic acid production under anaerobic conditions by some ruminant microorganisms. This work aimed to investigate the feasibility of Actinobacillus succinogenes to ferment C6 sugars into succinic acid. Kinetics and yields of succinic acid production with variant sugars concentration in the relevant synthetic medium were tested. For an equal mixture of glucose and fructose used as substrate at 0.4 M, and under proved optimal conditions (pH 6.8, T= 37 °C, sparging with N2 for 5 min and 1 % of biomass), 0.28 M of succinic acid were obtained. This concentration corresponding to a yield of 0.58 (mol of carbon of succinic acid per mol of carbon of sugar consumed anaerobically) and volumetric productivities of 0.27 g/L · h. All yield and concentrations obtained were significant and in order of what is reported in the literature.

Iron-Catalysed Reductive Amination Reactions to Access Cyclic Amines 15:30

Wei D.[1], Netkaew C.[1], Carré V.[1] and Darcel C.[1]
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Iron catalysis has seen an impressive breakthrough during the last two decades, and iron can now be considered as a valuable alternative transition metal for organic synthetic transformations. [1] More precisely, in the reduction area, it became an efficient player for the selective reduction of olefins, alkynes, carbonyl and carboxylic derivatives, imines and nitro compounds. [2] On the other hand, in molecular chemistry, multi-step and multi-component transformations lead to really attractive, efficient and sustainable technologies, avoiding several steps of work-up and purification of intermediates. [3]
Lately, we have shown that reductive amination of levulinic acid, 1,5- and 1,6-keto acids with amines [4] and reductive amination of carbonyl derivatives with ω-amino fatty acids [5], leading to pyrrolidines, piperidines and azepanes, catalyzed by iron NHC (*N*-Heterocyclic Carbene) complexes under both visible light irradiation and thermal conditions, by means of hydrosilylation reactions (Figure 1).

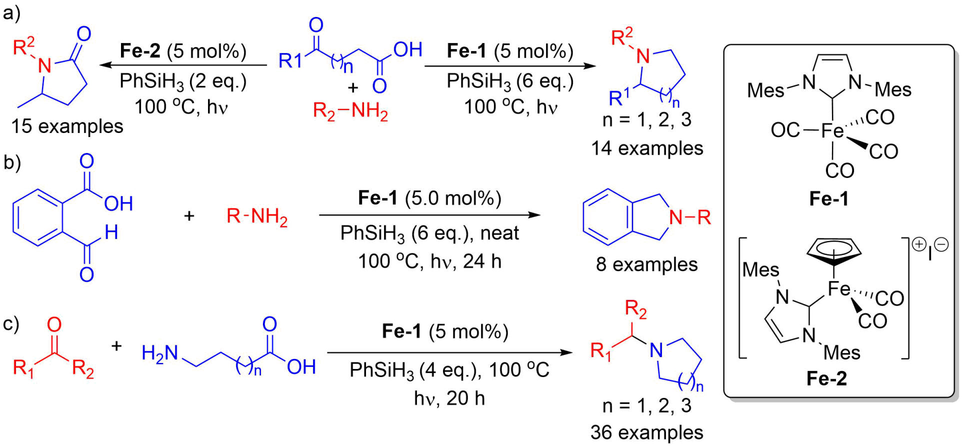

Figure 1 – Iron-catalysed reductive amination reactions to access cyclic amines.

A selective production of pyrrolidines *vs* pyrrolidinones *via* hydrosilylation of levulinic acid by switching of the iron complexes from **Fe-1** to **Fe-2** is presented in Figure 1a. The reactions proceeded efficiently with various amines in isolated yields up to 93%. Noticeably, under similar conditions, cyclic amines such as piperidines and azepanes were efficiently synthesized with yields up to 92%, by reaction of anilines with 1,5- or 1,6-keto acids, respectively. Similarly, *N*-arylinsolidoline compounds can be prepared from 2-formylbenzoic acid in 57-93% yields (Figure 1b). [4] Then the complex **Fe-1** showed also good performances for the preparation of *N*-substituted cyclic amines (including pyrrolidines, piperidines, azepanes) starting from ω-amino fatty acids and a variety of carbonyl derivatives, with 36 examples, 47-97% isolated yields (Figure 1c). [5]

[1] C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217.

[2] D. Wei, C. Darcel, *Chem. Rev.* **2019**, *119*, 2550.

[3] a) D. Wei, C. Netkaew, C. Darcel, *Eur. J. Inorg. Chem.* **2019**, doi: 10.1002/ejic.201900122; b) J.-L. Renaud, S. Gaillard, *Synthesis* **2016**, *48*, 3659; c) B. Trost, *Science* **1991**, *254*, 1471.

[4] D. Wei, C. Netkaew, C. Darcel, *Adv. Synth. Catal.* **2019**, *361*, 1781

[5] D. Wei, C. Netkaew, V. Carre, C. Darcel, *ChemSusChem* **2019**, doi: 10.1002/cssc.201900519

15:45

High performance dense proton ceramic electrolyte material obtained by Cold Sintering Process

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Sintering thermal treatment of ceramic materials used for fuel cells (SOFC) is a crucial step to densify and improve material properties. However, many sintering processes involve relatively high temperature range. For refractory material, the densification process is energy consuming, as it performed at temperature higher than 1200°C and requires several hours to achieve sufficient density. Recently, a novel sintering process named cold sintering (CSP) has been developed and applied to large range of materials [1]. This new technique, derived from the hydrothermal method, can achieve dense ceramics material at low temperature using a small volume of liquid phase to enhance densification through dissolution-precipitation mechanism under uniaxial pressure during a short time period [2]. $\mathrm{BaCe}_{0,8}Zr_{0,1}Y_{0,1}O_{(3-\delta)}$ BCZY, is well known as electrolyte for proton ceramic fuel cells (PCFC) but they require high sintering temperatures ($\approx$ 1600°C) and suffer from intrinsic grain boundaries resistance. In this study, we search to reduce the densification temperature of the BCZY electrolyte material by applying the cold sintering process at a temperature $<$ 200°C. A number of sintering parameters is studied to optimize and accomplish CSP, such as quantity of solvent, temperature and pressure. Experimental results show a significant improvement of the relative density, which increases from 66 % for a reference sample prepared without water addition to 83% after cold sintering at 180°C. A post annealing treatment at 1200°C, which is at least 200°C lower than conventional sintering, was found to be an essential step to a further densification improvement (93% of relative density). Electrochemical properties studied through electrochemical impedance spectroscopy show a conductivity of about 410^{-3} $S.cm^{-1}$ after cold sintering, then reaches a value of 2.310^{-2} $S.cm^{-1}$ after a post heat treatment. The morphology was investigated to establish a correlation between the electrochemical behavior and the microstructure of materials. The cold sintering could be an alternative route to accelerate densification process and lower the temperature while perceiving excellent properties of the material.

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Selective functionalization of cyclic imides and amides with ruthenium catalysts

16:00

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Cyclic imides and amides are one of the most widely used functional groups in chemical synthesis and they are also present in many relevant molecules from pharmacology to materials sciences.[1] As such, the development of selective and efficient functionalizations within this backbone is highly attractive although it remains scarce to date.[2] In this contribution, I will show the use of benchmark and robust ruthenium catalysts to tackle unprecedented transformations with cyclic a/imides. In particular, we have found a single step protocol leading to amides starting from phthalimides via selective scission of C-C and C-N bonds with unexpected CO2 release.[3] Furthermore, I will present the first use of cyclic amides as weak directing groups in transition metal-catalyzed C-H bond functionalizations. Regio- and site-selective hydroxylation and alkenylation reactions have been accomplished, including the late-stage derivatization of a drug.[4]

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Amphithéâtre Pascal
Pascal Amphitheatre

Hybride photonic integrated circuit based on porous silicon and polymers materials for sensing applications “HYSIPOP”

11:15

Cassio F.[1], Lorrain N.[1], Poffo L.[1] and Guendouz M.[1]
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The HYSIPOP thesis aims at producing a prototype of an ultra-sensitive integrated optical biosensor for detecting specific low-level biological molecules involved in prostate cancer. The detection at early stages of specific biomarkers of this disease such as PSA (Prostate-Specific Antigen) will allow to quickly implement treatments to prevent the containment of this disease.

The integrated optical biosensor will be made of a porous material with large surface area which allows the grafting of specific molecules after functionalization steps. The use of a porous material as optical transducer offers the advantage of a more sensitive detection of molecules than with a bulk material because the interaction of the light with these molecules takes place in the volume (heart of the porous structure) and not by evanescent mode.

The optical detection function will be ensured by resonant waveguiding structures such as micro-resonators in which light propagates and allows only certain wavelengths, so-called resonant. The presence of molecules in contact with this type of sensor will cause a shift in the resonance wavelength. Thus, by measuring this wavelength shift, it will be possible to estimate the concentration of specific molecules grafted on the porous silicon surface.

In order to improve the sensitivity and the lowest detectable concentration of the system, a Vernier effect structure will be performed. In this structure, a reference micro-resonator will have to be cascaded to another one that will be sensitive to the presence of specific molecules grafted on the inner surface of the porous material. Then, the induced phenomena will amplify the range between two resonance wavelengths, which will enhance the sensitivity of the system. A microfluidic system will have to be adapted to the optical structure to allow *in situ* detection on the optical characterization bench.

However, losses in porous silicon based waveguides are more significant than in bulk materials due to the porosity. This suggest the use of low propagation loss polymer waveguides in the part of the structure which are not in contact with the molecules to be detected. The whole Vernier effect structure will then be constituted by the two cascaded micro-resonators, the reference micro-resonator will be made in SU8 polymer and the sensing micro-resonator will be made in porous silicon material. In order to ease the coupling between the polymer and the porous silicon waveguides, tapers will be implemented.

11:30
Probing bonding in trihalogen compounds involving astatine by ELF and QTAIM topological analyses: a multiconfigurational and relativistic approach

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Chemical bonding is one of the central concepts in Chemistry. Nevertheless, it does not correspond to a measurable quantity and it remains in consequence as a fuzzy concept. In Quantum Chemistry, many theoretical models and derived computational tools have been developed so as to get insights about it; however, most of them neglect or do not sufficiently take into account relativistic effects, even for heavy-element systems. Different efforts are worth being noted [1,2], but they are restricted to single-determinant quantum chemical methods. Thus, our objective is go beyond this approach and describe bonding from multiconfigurational and relativistic calculations[3].
This presentation will be only focus on topological analyses by means of the so-called Quantum Theory of Atoms In Molecules (QTAIM) [4] and the analysis of the Electron Localization Function (ELF) [5]. To illustrate the use of our approach, the bond of the experimental evidence anions AtX_2^- (X=Br, I) and $BrAtI^-$[6] will be discussed and compare to the ones that occur in the full series of dihalogen compounds of the AtX (X=At, I ,Br, Cl and F) type. Results reveal that: *(i)* there is a weakening of the *classical* covalent character in the trihalogen compounds and *(ii)* the ternary one effectively behaves as a centrosymmetric trihalogen. This latter behaviour could not be anticipated without the help of the present quantum chemistry calculations and bonding analyses, which clearly illustrates the potential of the developed methodology for understanding the chemistry of rare elements such as astatine.

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

11:45

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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].

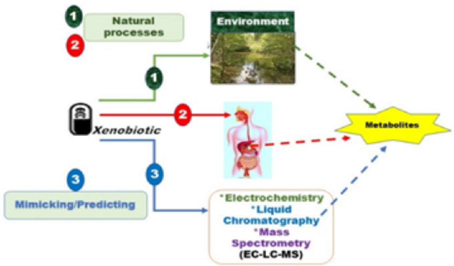
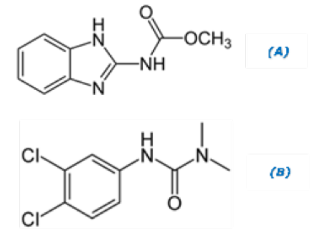


Figure 1: Metabolic pathways of a xenobiotic



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.

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12:00

Water Vapor Binding on Organic Matter-Coated Minerals

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Atmospheric water vapor binding to soils is a key process driving water availability in unsaturated terrestrial environments. Using a representative hydrophilic iron oxyhydroxide, this study highlights key mechanisms through which water vapor (i) adsorbs and (ii) condenses at mineral surfaces coated with Leonardite humic acid (LHA). Microgravimetry and vibrational spectroscopy showed that liquid-like water forms in the three-dimensional array of mineralbound LHA when present at total C/Fe ratios well exceeding $\sim 73\,\mathrm{mg}$ C per g Fe (26 C atoms/nm^2). Below these loadings, minerals become even less hydrophilic than in the absence of LHA. This lowering in hydrophilicity is caused by the complexation of LHA water-binding sites to mineral surfaces, and possibly by conformational changes in LHA structure removing available condensation environments for water. An empirical relationship predicting the dependence of water adsorption densities on LHA loadings was developed from these results. Together with the molecular-level description provided in this work, this relationship should guide efforts in predicting water availability, and thereby occurrences of water-driven geochemical processes in terrestrial environments.

Advanced high-field and benchtop NMR methods for lipid profiling and monitoring of microalgae

12:15

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Microalgae are increasingly studied in both academy and industry owing to their broad applicative potential. Indeed, they are able to create biomass with significant productivities compared to traditional crops. Besides, there is a great biodiversity in microalgae and some species can produce valuable compounds in an ecological way, since microalgae consume CO_2, a highly emitted gas largely involved in the greenhouse effect.

Lipids are important molecules in the list of valuable compounds produced by microalgae. They can be used in food industry or for biofuel production. Some species of microalgae have the ability to produce reserve lipid –mainly triglycerides– under nitrogen starvation conditions: microalgae are then disrupted and a metabolic shift is provoked. In order to better understand this phenomena and find the best way to produce lipids, biological and process research works are carried out by a substantial research community.

NMR has a great potential to study the lipidic metabolism of microalgae in a non-destructive and reproducible fashion. In this context, we aim at bringing some of the most recent NMR developments into the bioprocess community, in order to maximize the observable information. On the one hand, advanced high-field NMR methods offering the best performance in sensitivity and resolution are investigated for the lipid characterization of microalgae extracts. Different NMR quantitative approaches (^{1}H NMR, ^{13}C NMR and our recently developed quantitative 2D NMR methods [1]) are evaluated in this study in terms of analytical performance and available information on lipids.

On the other hand, we investigate the potential of recently developed benchtop NMR spectroscopy [2] as an online lipid sensor. We demonstrate the potential of this transportable setting for the real-time and in vivo monitoring of microalgae cultivations. Thanks to the implementation of advanced solvent suppression NMR pulse sequences [3], a lipid peak can be obtained and integrated in order to monitor the lipid concentration in real time, in a flow-compatible and non-invasive way. This is then demonstrated with a coupling with a real microalgae cultivation system (photobioreactor).

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12:30

Impact of confinement on the properties of ionic liquids in controlled meso-porosity silica matrix

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Ionic liquids are salts commonly told to melt at temperature below 100°C. At room temperature, they are liquid, totally composed of ions. Specific features are low flammability, very low vapor pressure and high thermal stability, and also a large window of electrochemical stability [1]. They can be used as alternatives to organic solvents and are studied to replace (totally or partially) the organic electrolytes currently used, for instance in energy storage devices. The use of ionic liquids could be facilitated by integrating them into solid devices able to maintain their liquid properties, such as ionogels [2]. An ionogel is a biphasic material consisting mainly of a liquid phase, the ionic liquid, which is confined in a solid porous matrix (organic, inorganic or hybrid). Under good conditions, the ionic conduction properties of an ionogel are close, or even improved [3], to those of the unconfined ionic liquid. It has also been observed that the confinement of an ionic liquid can lower its melting temperature, which makes it possible to maintain good ionic conduction properties even at low temperatures [1].

The aim of the current works is to understand the effects of confinement on the physico-chemistry of ionic liquids, specifically by the study of phenomena at the interface. The structure of the confining network (organic, inorganic or hybrid type) must be controlled to study its impact on the confinement of ionic liquids (coll. A. Galarneau, Montpellier). We will focus more particularly on the pore size and the chemical nature of the species on their surface. The ionic liquids are chosen according to their chemical properties (protic, aprotic, coll. A. Balducci, Jena, Germany) and their structure, in order to highlight the impact of a modification of the chemistry or the conformation of the system. Raman spectroscopy shows modifications of the ratio of the cis-trans conformations of TFSI anions. Depending on confined ionic liquids, modification of phase transitions are observed as well as an increase of conductivity increasing the meso-porous size. Adding Li^+ limites or suppresses those effects. The confinement shows a decrease of the coordination number of Li^+ by TFSI, thus allowing an enhancement of lithium cation dynamics.

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What only SMAUG can see

14:45

Dudás E.[1], Charles C.[2], Kassi S.[3], Kulkarni V.[4], Benidar A.[1] and Georges R.[1]

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How can we characterise molecules that are unattainable due to their astronomical distance from the Earth? The SMAUG apparatus (*Spectroscopy of Molecules Accelerated in Uniform Gas flows*) was developed to reproduce some aspects of hot planetary atmospheric environments, for example those that surround hot Jupiters or cool carbon evolved giant stars, which reach temperatures up to 2500 K.

In the laboratory astrophysics group of the Institute of Physics of Rennes we coupled an ultrasensitive cavity-ring down spectrometer with a hypersonic jet mixture of argon and small hydrocarbon molecules. The gas mixture is heated up to 2000 K before being accelerated through a carefully designed graphite Laval nozzle. In the resulting non-divergent uniform flow we can distinguish a high-velocity isentropic core from a surrounding hot and low velocity shear layer. In the isentropic core, the molecules are in non-local thermodynamic equilibrium conditions because the rotational temperature equilibrates rapidly down to the translational temperature of the flow which is close to 10 K, while vibrational temperature does not relax and remains very close to the initial temperature. This strong decoupling of the internal degrees of freedom of the polyatomic hydrocarbon molecules results in a simplified rotational structure of their infrared spectrum (1,5 µm range) without depopulating the highly excited vibrational energy levels. It allows us to better understand the hot band structure of the studied molecules suspected to play a major role in the thermal structure of the atmosphere of hot Jupiters.

This original experimental approach will be presented with preliminary results for methane.

15:00

Alkaline-earth carbodiimides as new potential phosphors for white LEDs

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Light-emitting diodes (LEDs) are emerging as indispensable solid-state light sources for the next generation of lighting. In this current era of energy saving and sustainable development, LEDs represent a green alternative to other lighting systems used nowadays. In particular, LEDs have some advantages over fluorescent and incandescent lamps: besides a better lifetime and a reduced operating voltage, they do not emit strong UV radiations, are mercury-free and almost fully recyclable.

Nowadays, conventional white LEDs are made up of a blue GaN/InGaN LED chip (460 nm) covered with a yellowish emitting phosphor, cerium(III)-doped yttrium aluminum garnet ($Y_3Al_5O_{12}$:Ce^{3+}, YAG:Ce). Combining these two colors yields white light. Nonetheless, the light produced by such device lacks some red emission component which results in a bad rendering of the colors of the illuminated objects. To overcome these problems, the development of red and green phosphors that can be excited by blue or ultraviolet light-emitting diodes has been largely investigated within the past decade. In particular, nitrides and oxynitrides materials have been widely studied as they present specific properties induced by nitrogen such a greater covalent character compared to oxides. This leads to an increase of the crystal-field splitting of the 5d levels resulting in a shift of the emission towards higher wavelengths when Eu^{2+}, Ce^{3+} or Mn^{2+} luminescent centers are involved [1, 2].

This work will focus on another group of nitrogen-containing compounds, i.e. alkaline-earth carbodiimides, in order to explore their potential as hosts for luminescent centers. A new facile synthetic route involving carbon nitride (C_3N_4) has been developed for the preparation of such compounds and will be illustrated by few examples such as $CaCN_2$ and $SrCN_2$. Structural characterizations and optical properties of Mn^{2+}, Ce^{3+} doped $CaCN_2$ as well as the effect of Ca/Sr substitution on the emission behaviour will be investigated on the bases of high-resolution X-ray powder diffraction and photoluminescence analyses to evaluate the potential of such systems as red-phosphors.

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Optimization of Si/Gr Based Anode Formulation for High Energy Density Li-Ion Batteries

15:15

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In need of increasing automotive applications, it is necessary to find both higher capacity and higher-capacity retention electrode materials for Li-ion batteries. Among the candidates for negative electrode [1], silicon appears as an attractive alternative to graphite due to its natural abundance, high specific gravimetric capacity (3579 mAh.g^{-1} vs. 372mAh.g^{-1} for graphite) and a large volumetric capacity (2081 mAh.cm^{-3} vs. 779 mAh.cm^{-3}). Silicon based electrodes nevertheless suffer from poor cyclability usually due to dramatic volume expansion of the electrode during the cycling and electrolyte reduction [2]. As a consequence, irreversible capacity losses are not limited to the first few cycles, but may continue to deteriorate cell performance and life [3, 4].

On one hand, previous studies demonstrated that the formulation [5], the processing [6] of the composite electrode and the adhesion to the current collector are critical for Si with respect to the electrochemical performance. The design of a flexible network of shaped conductive additives bonded with an aqueous binder to silicon particles through an optimized ratio of covalent and hydrogen bonds greatly help in facilitating a homogeneous functioning of the electrode that minimizes electrolyte reduction and keep the mechanical integrity of the electrode. On the other hand, using a combined silicon/graphite material also help in mitigating volume variations expected to occur upon cycling, especially for high mass loading electrodes (>3-4 mg/cm^2).

In this study, we use both approaches by tuning the binder incorporation in the case of a 50/50 wt Silicon/Graphite composite electrodes. We focus here in particular on the electrode formulation, using a polyacrylic acid polymer binder thanks to its grafting mechanism to silicon particles enabling a strong mechanical cohesion even in the case of high-loaded electrodes. [7] pH and viscosity adjustments of the electrode slurry will be discussed, as they seem to have a remarkable effect at the interface between electrode and current collector. In fact, the longer drying process (due to thicker coating) exacerbate different corrosion mechanisms and migration phenomena that were not observed previously for thin electrodes usually studied. Characterizations on this interface were carried out, combining XPS and SEM, in order to offer a further comprehension of Si/Gr cycling performance as a function of electrode preparation.

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Layered double perovskite: in situ growth of Co–Ni alloy nanoparticles as a catalyst for efficient SOFC anode

15:30

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Solid oxide fuel cells (SOFC) are capable of converting various fuels (H2, syngas and hydrocarbons) directly into electricity with high efficiency and low emission [1-6]. However, the application and commercialization of SOFC technique are currently limited by high cost and insufficient reliability of its components (cathode, electrolyte and anode) induced by high operating temperature, sealing problems in fabricating hermetic/stable stacks [7], redox instability as well as coking/sulfur poisoning in anodes [8-9]. Therefore, the design and exploration of redox stable and coking/sulfur resistant anodes are one of active areas in SOFC research [3,10]. Perovskite La0.75Sr0.25Cr0.5Mn0.5O3-d [11] and layered double perovskite PrBaMn2O5+δ [12] have been proved to be promising anode materials with redox stability and improved coking and sulfur resistance under SOFC anodic operating conditions. However, they still suffer from low electrical conductivity and/or poor electrochemical activity for oxidation of fuels, especially at intermediate temperature range (600 to 800°C). Recently, the demand for active nanoparticles with multiple functionalities in catalysis has increased, so exsolutions of intermetallic nanoparticles could be an effective strategy to meet the requirements. In situ exsolved nanoparticles on metal oxide materials have received much attention in catalysis due to their well socketed structure and high catalytic activity. The anodes were fabricated through reducing perovskite precursors and in situ exsolving metal/alloy nanoparticles from oxide matrix [12-13]. Herein, we report exsolved Co–Ni alloy nanoparticles formation in a NdBaMn1.9Co0.05Ni0.05O5+δ layered double perovskite. In situ precipitation of the Co-Ni alloy nanoparticles at the surface of the layered oxide were carried out under humidified (3% H2O) H2/Ar at 800°C. Structure, morphological and composition characterizations of the oxide materials before and after exsolution were examined using various techniques (X-ray diffraction, electron microscopy, XPS). To confirm the catalytic effect of the exsolved nanoparticles, the electrochemical performance of single cells is being tested using various electrolyte-supported cell in humidified H2 (3% H2O) as the fuel and ambient air as the oxidant.

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15:45

First-principle Investigation of the Double ESIPT Process in a Thiophene-based Dye

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Excited-State Intramolecular Proton Transfer (ESIPT) is a process widely studied during the last decades. The interest for ESIPT dyes in OLEDs, laser dyes and fluorescent probes originates in their fluorescence properties. Depending on the stabilities of the tautomers in their excited state (ES), an intramolecular proton can rapidly occur and yield to the so-called keto tautomer. If optical spectroscopies allow observing this behavior, theoretical calculations are helpful to rationalize this transfer by exploring the stabilities of the different ES. For the unusual emission spectrum of 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol (BBTP), the complexity of the emission spectrum is due to the presence of two ESIPT sites that give rise to three non-equivalent tautomers. The different maxima were experimentally attributed to the initial double enol form, the single ESIPT enol–keto tautomer, and the double ESIPT structure [Y. Hao and Y. Chen, Dyes Pigm., 2016, 129, 186 – 190]. Our simulations, based on Time Dependent Density Functional Theory (TD-DFT) and post Hartree–Fock methods [ADC(2) and CC2] coupled to different schemes to include solvent effects, are able to reproduce all key experimental outcomes. Moreover, we are able to lift the inconsistencies present in earlier theoretical studies by using a state-specific solvation model. Finally, using a validated model, we explore the impact of substitution (donor and acceptor groups) on the ESIPT process [1].

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Asymmetric Synthesis and Biological Evaluation of New Amino acids and Oxaproline-Based Tripeptides

16:00

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Up to 200 million individuals of world individuals are suffered from HCV. In approximately 80 percent of cases, HCV infection leads to a chronic form of hepatitis “fibrosis” which is incurable in between 40 and 60 percent of patients. In Egypt HCV and its resulted long-term consequences, is a major endemic medical health problem. In 2008 having taken a representative random sample of the country, from different areas, an Egyptian study known as the Egyptian Demographic Health Survey (EDHS) informed that about 15 percent of the population have been infected, making this the highest prevalence in any population in the world. With highly occurrence rates between 2 and 6 per 1000 every year, that leads to an estimated 170,000 new cases every year to add to the 11.5 million patients suffering from the disease [1]. In the huge and recent therapeutical development of new anti-HCV drugs, a variety of active protease inhibitors have been either already approved for treatment of HCV in some countries (boceprevir, telaprevir) or are under current clinical trials (Phase III : faldaprevir, asunaprevir, simeprevir; Phase II : danoprevir, vaniprevir) [2]. These members of the "previr" family display a common structure based on a tripeptide featuring a central 4-heteroarylproline unit, as exemplified by asunaprevir [3]. Our project aims to the synthesis of new analogues of asunaprevir which will be evaluated as novel anti-HCV agents. These new analogues will involve isosteric replacement of proline ring with isoxazolidine ring and introduction of different heteroaryl appendages at the C4 position. The oxaproline precursors will be de novo synthetized using an asymmetric 1,3-dipolar cycloaddition (DC) strategy, this involves the reaction between N-heteroaryl ethers and nitones [4]. The obtained oxaproline unit will be conveniently subjected to sequential deprotection of N- and CO2H groups, and amide couplings to afford P2-P3 and P2-P3-P1 fragments, respectively. This PhD project includes two domains of methodologic research in organic chemistry: (i) the control of diastereoselectivity in pericyclic reactions, here between heteroaryl vinyl ethers and functional nitrones (ii) the synthesis and the coupling of new optically active non-natural and «difficult to make» amino acid derivatives.

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Amphithéâtre Besse
Besse Amphitheatre

Clogging dynamics of a single pore by colloidal particles

11:15

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The transport of dilute colloidal suspension through a porous medium like a filter or a soil, leads to the formation of clogs. Clogging is a complex process depending of hydrodynamics and physicochemical parameters including the nature, the size and the surface charge of the particle or the ratio particle size over pore size. Thanks to microfluidics, transparent porous media have been designed and allow monitoring the clogging process at the pore scale. Investigating the transport of particle such their deposits or capture by the pore walls enables understanding the partial or total clogging conditions. However, the clogging dynamics has not been studied also its impact on the velocity field of the whole porous medium.

Our works tends to understand this dynamic at the pore scale to predict clogging in the whole porous medium. In a single pore, we investigate the modification of the hydraulic resistance due to the particle deposit on the velocity field. Particle tracking all along the clog formation provides several physical parameters like the volume fraction, the particles velocity and so enable us to estimate the hydraulic resistance considering the Darcy law. By varying physicochemical parameters such as the size, the surface charge and the nature of the particle, we identify how these parameters impact the hydraulic resistance, i.e., their impact on the variation of the flow condition.

11:30

Osteosarcoma, structure and simulation

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Osteosarcoma is a malignant bone tumor characterized by an invasive bone and tumor growth that mainly affect teenagers and young adults. It requires extremely invasive surgery to extract, and still displays a high mortality rate two years after removal. Bone tumor offers a structure that can be studied through physics science means, and using those we strive to study this kind of tumor using new approaches. First, by focusing on the short development times, by opposition to biology's approach of studying well-developed long times samples. Second, through the use of a cellular automaton, by seeking to reproduce the osteosarcoma's structure using only simple laws, thus enabling us to to determine the propagation mechanism.

Ligands multifonctionnels à base de terpyridine et leurs complexes : Synthèses et propriétés

11:45

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We report here the synthesis, characterization and physicochemical properties of multifunctional ligands and their metal complexes. A first family of ligands has the following pattern TTF-(π)-Terpy where tetrathiafulvalene is used as electron-rich electroactive unit. A second family of ligands based on the benzothiophene motif (Bz-(π)-Terpy) where the benzothiophene is interesting for its luminescence properties. Terpyridine is used as a chelation unit for various metal cations with access to metal complexes with an original structure and electronic properties 1. We will also study the influence of the metal cation on the different electro (optical) properties and in particular in Non Linear Optics as previously shown in our laboratory with multifunctional ligands based on the TTF.[1,2] Concerning the metal complexes derived from the TTF, they will be used as precursors for the preparation of radical cation salts using the electro-crystallization technique in order to obtain (semi) conductive materials.

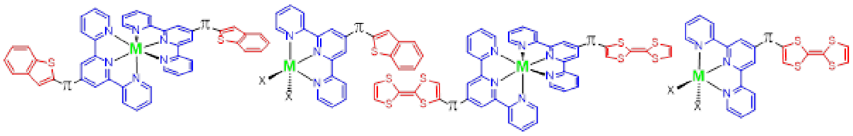

Figure 1 – Targeted heteroleptic and homoleptic mononuclear complexes

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12:00

New Fluorenyl Porphyrins for TPE PDT applications

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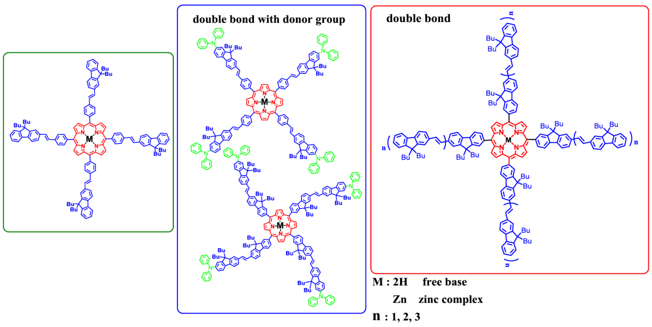
Since 2004, we are interested in the optical properties of fluorenyl-porphyrins because we found that TFP, a porphyrin possessing four fluorenyl arms [1], exhibits a high fluorescence quantum yield (0.24) compared to the reference tetraphenylporphyrin (TPP), demonstrating the good capacity of the fluorenyl units to enhance fluorescence quantum yields. [2-6] So first, we synthesized a series of porphyrin dendrimers with fluorenyl arms connected by non-conjugated ether linkers. [7] In 2016, to improve these systems, a second group of porphyrin dendrimers fully conjugated with alkynyl linkers was obtained (Triple Bond as described in Figure), and their photophysical properties were ameliorated. [5] Very recently, to improve these Triple bonded systems, Double bonded porphyrins are elaborate because of better conjugation than triple bond porphyrins. [8] Based on TFP, we designed a series of new porphyrin compounds containing a larger number of fluorenyl antennae connect by various linkers, in order to make these porphyrins appealing for 2-photon based photodynamic therapy (PDT) and bio-imaging.



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A new liquid crystal phase: Characterizations and applications

12:15

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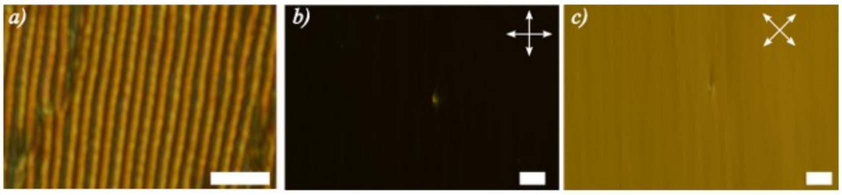
Liquid crystalline mesophases (LC) are intermediate states of matter between the liquid and solid phases. The Nematic and Smectic phases are the two main common LC mesophases, often observed when heating organic compounds consisting of rod-like molecules. The Nematic phase is known from long time, being at the heart of liquid crystal displays (LCD) technologies. A new LC phase called Nematic Twist Bend (NTB)[1], was theoretically predicted in 2001 by I.DOZOV[2]. This was experimentally evidenced by X-rays diffraction (XRD) in 2010. Sharing some features of Nematic and Smectic phases, it is formed by achiral, curved shape molecules that yield a spontaneous helicoidal structure with a pitch of order nanometer. The response time of the NTB phase to an electric field is a thousand time faster than the usual nematic, which make this phase, promising for optical application. The study of NTB phase and their potential in new applications require i) to reduce the temperature range of this phase, often found above 100°C and ii) to master their alignment at large scale, i.e. their orientation by solid substrates. During the first part of my PhD at laboratory Charles Coulomb à Montpellier, I designed a mixture of molecular compounds that provides a NTB phase at room temperature. The phase diagram was established using polarized optical microscopy, XRD and differential scanning calorimetry. I also characterized more deeply the thermodynamic, optical and elastic properties of the phase. I also improved the second point by elaborating new aligning layers on glass that provide different anchoring conditions. I studied the influence of these substrates used for designing thin liquid crystal cells (1 μm thick) and finally obtained for the first time a good spontaneous orientation of the NTB phase .



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12:30

Synthesis of Luminescent Molecules Based on triazinane-2,4,6-trione and study of their OPTICAL properties

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

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

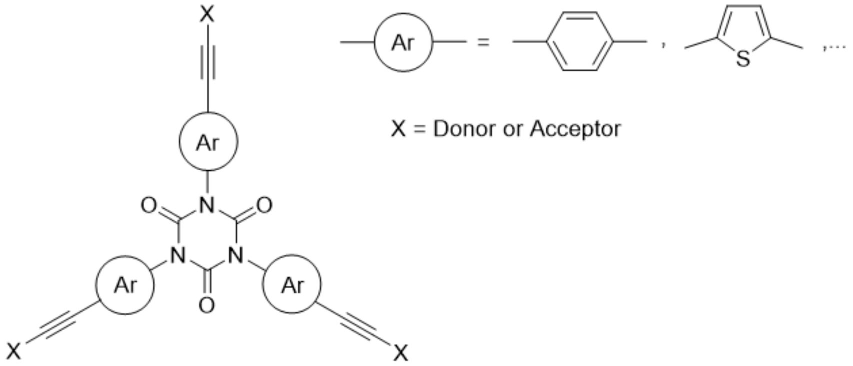

Figure 1 – Molecular Structures of isocyanurate-cored chromophores.

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Side-bridged pyclen ligands: a new family of reinforced tetraazamacrocycle for transition metal coordination

14:45

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[2]Department of Inorganic and Analytical Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem tér 1, H-4032 Debrecen, Hungary,
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Among various chelating agents, macrocyclic ligands such as polyazamacrocycles, judiciously functionalized, are known to strongly bind a large variety of metals. This ability gives them many potential applications especially for both diagnostic and therapy of cancers. Moreover, reinforced macrocycles constrained by an ethylene bridge between two adjacent (SB for side-bridged) or opposite (CB for cross-bridged) nitrogen atoms, have demonstrated their excellent coordination properties. Indeed, this class of ligands exhibits unusual acid-base properties, redox behavior and has revealed a particular predisposition to form kinetically inert metal complexes due to the steric congestion imposed by the ethylenic bridge.[1] While cyclen and cyclam reinforced derivatives are well known in the literature, we developed for the first time an innovative synthesis pathway of side-bridged pyclen.[2] This adds even more rigidity to this macrocycle that contains an aromatic pyridyl group in its backbone. Our strategy is based on the reduction of pyclen-oxalate, an essential intermediate for the regiospecific functionalization of non-symmetric pyclen-based derivatives (Figure 1).[3,4] Different N-functionalized side-bridged pyclen ligands and their non-reinforced analogues have been synthetized (Figure 1) for the coordination of transition metals such as Zn^{2+}, Cu^{2+} and Mn^{2+}. The properties of the complexes were deeply investigated focusing on the kinetic inertness of the reinforced complexes. In addition, relaxometry studies have been performed in order to determine the potential of the Mn^{2+} complexes as contrast agents for MRI applications.

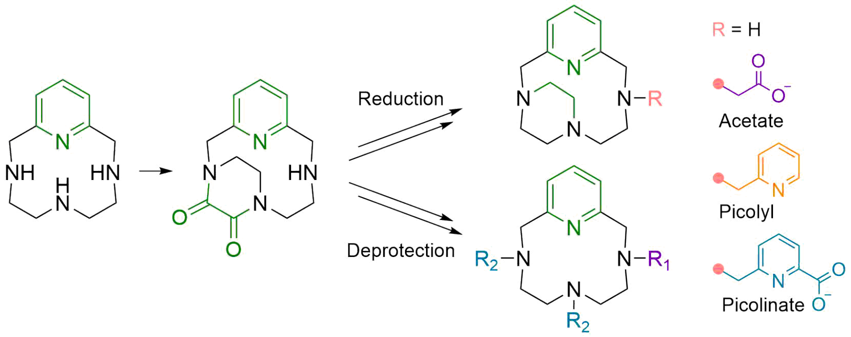

Figure 1 – pyclen and SB-pyclen regiospecific N-functionalization.

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15:00

Correlated Metal Phase Creation by Electric or Light Pulses in Mott Insulators

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The discovery of an Electric Mott insulator to metal Transitions [1,2] (EMT) have launched strong debates about physical mechanism driving this process [3–5]. Recently, a mechanism based on an old prediction of Fröhlich6 was proposed, involving the massive promotion of hot electrons by electric field and an electronic avalanche effect related to the divergence of electronic temperature [7]. In parallel, different studies have demonstrated that the EMT was not spatially homogeneous, but corresponds to the creation of a percolating and conducting filamentary path [6].

Despite these recent progresses, some fundamental questions regarding the physics of the EMT remain unsettled. On the one hand, the Fröhlich model suggests the existence of new appealing properties, such as a synergetic effect of electric and laser pulses. We have tested this opportunity by performing pump-pump-probe experiments on single crystals of the Mott insulator $GaTa_4Se_8$, whereby electric pulse and controllably delayed laser pulse simultaneously excite the crystal while electric probe monitors its conductivity. Preliminary results, obtained at different laser wavelengths but with comparable number of photons per pulses, seem to confirm the hot carriers generation mechanism. These results will be presented along with complementary calculations estimating the trivial thermal effects. On the other hand, the nature of metallic phases created within the conductive filaments during the EMT is still unclear, both from theoretical and experimental viewpoints. Some results point indirectly to a strong similarity with the Correlated Metal phase obtained under pressure. However, no direct structural evidences of such a compressed metallic phase induced by the EMT in Mott insulators were obtained so far. We will present a Raman and conductive AFM investigation of the metallic filamentary paths, performed in parallel with a Raman study of the pressure-induced insulator to metal transition on the canonical Mott insulator $(V_{1-x}Cr_x)_2O_3$.

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$BiVO_4$ photoanodes prepared by alkaline electrodeposition, enhanced with Fe co-catalysts for solar water splitting

15:15

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Hydrogen (H_2) is a very promising energy carrier for the future. [1] Water electrolysis, triggered by a renewable source of energy (such as sunlight), can be employed to obtain pure H_2 without carbon emissions. [2, 3] This process can be conveniently carried out by photoelectrochemical cells, devices composed of light-absorbing semiconductors interfaced with co-catalysts to efficiently split water under solar illumination. To make an efficient photoelectrochemical cell, it is important to use a photoanode (performing the oxidation of water to O_2 having a high conversion efficiency and based on abundant and inexpensive materials. Among many n-type semiconductors, bismuth vanadate ($BiVO_4$) has attracted a particular attention because of its suitable band gap (2.4 eV) and low valence band. [4–6] On the other hand, ($BiVO_4$) suffers from a poor charge carrier lifetime [7, 8] and a poor catalytic activity for water oxidation, which currently limit its photoelectrochemical properties. [7–10] We developed a new technique for electroplating Bi0 on an optically transparent conductive oxide surface from a highly alkaline solution. This layer can then be converted to ($BiVO_4$) but its performance as a photoanode is however, rather poor. In order to considerably improve the properties of this photoelectrocatalytic layer, we introduce a new simple and general method which allows coating BiVO4 with an amorphous FeOx catalyst layer, improving considerably its water oxidation efficiency, as demonstrated by a lower onset potential, higher photocatalytic currents and a decent stability (several hours). [11]

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15:30

$\beta-$**In$_2$S$_3$** for photovoltaic devices: investigation of the native point defects with *ab initio* first-principle calculations

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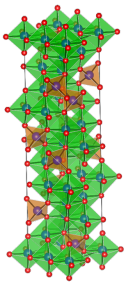
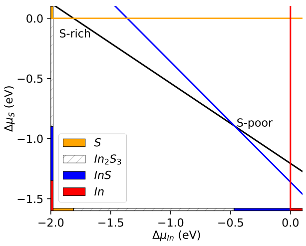
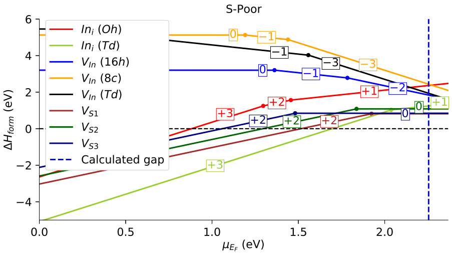
We report a theoretical investigation based on DFT calculations devoted to the nature of charge carriers in the $\beta-$In$_2$S$_3$ material used as buffer in chalcopyrite thin film solar cells. Our simulations led to unambiguous results concerning the incapability for this material to be a p-type semiconductor. Furthermore, it is demonstrated that the insertion of indium into a Td interstitial site seems to be the driving force leading to natural n-type conductivity. Our calculations took into account different atmospheres in order to be directly comparable with experimental data in particular the competitive InS structure was considered. It is shown that the S-poor condition strongly lesser the defect formation energy and should be privileged to achieve high free electron concentrations for potential applications. All the post-treatments were performed using the PyDEF 2.0 package.[2]



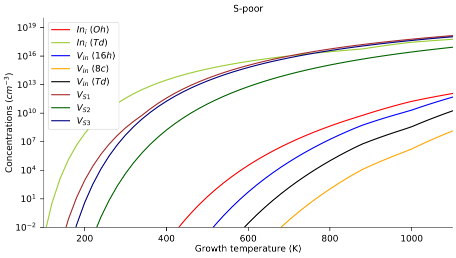
(a) $\beta-$In$_2$S$_3$ structure.



(b) Stability domain in ($\Delta\mu_{In}$, $\Delta\mu_S$) plane.



(c) Intrinsic defects formation enthalpies.



(d) $\beta-$In$_2$S$_3$ intrinsic defect concentrations.

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Solubilization of organic redox molecules in a mixture of an eutectic solvent and an aqueous solution: application to redox flow batteries

15:45

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Since the 2000's, the technology of redox flow batteries is in constant evolution. These systems produce powers of a few hundred kilowatts and can develop in a sophisticated arrangement a power of the order of megawatt with an operating time of up to ten hours. This last result positions them favorably to be coupled with the production of renewable energies by playing a buffer role in the energy distribution. Nevertheless, the current models are based on redox couples from ores and some of them are highly toxic (vanadium, zinc, chromium) [1]. To overcome this problem, a new design of redox flow batteries that use organic redox molecules has recently emerged [2]. Their diversity makes possible to target important criteria such as biodegradability and toxicity. However, in very high ionic strength aqueous solutions, these molecules suffer from a low solubility generally less than 0.1 mol.L-1. In this context, the project initiated by our laboratory proposes to develop a new generation of electrolyte solutions containing a deep eutectic solvent (DES) mixed with an aqueous solution. Given the number of molecules involved in the design of DES, each combination forms a solvent having specific physicochemical properties and characteristics such as ability to solubilize organic molecules or salts. As part of this study, the developed DES are hydrophilic in order to mix them with an aqueous solution (water + electrolyte) to ensure an ionic conductivity of at least 50 mS.cm-1. The organic redox molecules chosen as the active ingredient belong to the quinones family. This work describes the composition of the studied electrolytic solutions (eutectic solvent/aqueous solution) and their ability to solubilize the target redox organic molecules. These systems were then characterized by electrochemical analysis. The first tests performed in battery mode show the interest of these mixtures to diversify the nature of the redox molecules that can be used in redox flow batteries.

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16:00

Silica Hollow Core Antiresonant Fiber for Harsh Environment Mid-IR Sensing Applications

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There is a growing need for compact, fast and cost-effective sensors able to detect small traces of environmental pollutants and toxic vapors in a variety of atmospheric, security, healthcare, agri-food and industrial applications. Mid-infrared (mid-IR) spectroscopy is nowadays considered as a routine analysis and sensing tool providing highly discriminatory information on organic and inorganic molecules due to the excitation of vibrational and rotational transitions that are specific to these species. In particular, European aeronautic research program CleanSky2 strongly requests to detect critical molecules like CO_X, NO_X and H_2O, as well as other organic compounds and fire extinction agents.

Embedded gas sensing system for commercial aircraft engines requires a system compatible with the harsh conditions encountered around aircraft gas turbines. Silica fibers can withstand the high temperatures experienced in the exhaust gas of a reactor. However, as silica strongly absorbs at mid-IR wavelengths (about 2000 dB/m at 4.3 µm), hollow core antiresonant silica optical fibers (HC-ARFs) have been selected. In these fibers, mid-IR light is guided in the air rather than in the solid material and low propagation losses can therefore be achieved in a spectral region where silica would have been absorbent. Furthermore, the fabrication process of these fibers is similar to standard silica fiber or photonic crystal fibers (PCFs).

Simulations were performed to design hollow-core silica fibers transparent in the 4-5 µm region where combustion reaction gas products (CO_X, NO_X) strongly absorbs. In particular, an analytical model will be presented and compared to more sophisticated calculations based on Finite Element Method. Experimental characterization methods of hollow core silica optical fiber propagation losses will be discussed. Fiber attenuation lower than 1 dB/m at 4 µm were measured confirming the potential of these hollow core silica fibers for low range, high temperature deported CO_X sensing systems.

Forum
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Phthalocyanine dendrimers

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In 2004, we have reported the synthesis of porphyrin possessing four fluorenyl arms TFP [1-5]. Surprisingly, TFP exhibited a remarkably high quantum yield, compared to the reference tetraphenylporphyrin TPP demonstrating the capacity of the fluorenyl units to enhance quantum yields. Then, to exploite this efficiency, a series of porphyrin dendrimers bearing fluorenyl dendrons was prepared: new porphyrin OOFP possessing eighth fluorenyl pendant arms [6] and the SOFP possessing sixteen fluorenyl arms [6, 7].
As an applications, we next tested corresponding platinum(II) complexes in the fabrication of red Organic Light Emitting Diodes (OLEDs)[8-10]. Also, supramolecular assemblies possessing 12 or 24 fluorenyl arms, using these efficient building blocks have been obtained by our group [11]. Very recently we synthesised smaller units possessing 6 fluorenyl arms like dimers [10] as well as trimers [11]. Encouraged by these results, we will design Phthalocyanine macrocycles substituted by fluorenyls units.

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Stability enhancement of anchored dyes on mesoporous metal oxide electrodes upon crosslinking for photoelectrochemical devices

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The immobilization of dyes on nanocrystalline films of metal oxides has considerable implications for the development of innovative devices for photovoltaics, artificial photosynthesis, sensors and molecular electronics. For examples, they lie at the heart of dye sensitized solar cells (DSSCs) and dye-sensitized photoelectrosynthetic cells (DSPECs). These devices generally consist of a mesoporous film made of nanoparticles of a metal oxide coated with a monolayer of a molecular system. However, as far as the stability is concerned, the desorption of the dyes or of the dye-catalyst assembly from the metal oxide surface in electro- and photo-electrocatalytic systems still represents an important issue, which is far from being solved. Therefore, there is a real need for new approaches to improve the stability and lifetimes of photoelectrochemical systems. Towards this objective, we report in this study the crosslinking of the sensitizers with a thermally induced Huisgen 1,3-dipolar cycloaddition click reaction between an electron deficient alkyne and an azide, a strategy which we have employed before to crosslink non-linear optical chromophores into polymer matrices to stabilize their orientation into electro-optic devices.

We have shown that thermal copper free Huisgen reaction is a very simple reaction, which can be directly conducted on the dyes already anchored to a nanocrystalline film of a TiO2 or NiO electrodes. After crosslinking, the photoelectrodes keep their initial photoelectrochemical properties. More interestingly, the desorption of the immobilized dyes is heavily reduced compared to uncrosslinked films, highlighting thus the real potential of this strategy to maintain activity of photoelectrodes for applications where leaching of the dyes represents an issue. This is particularly valuable for photoelectrochemical devices such as DSSCs employing an aqueous electrolytes or for DSPECs in general.

Designing new titanium alloys for improved plasticity

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A new fast and reliable method to design beta titanium alloys displaying transformation-induced plasticity (TRIP) is proposed. The method relies on a thermodynamic and micromechanical model for the formation of martensite. It is assumed that martensite nucleation takes place through a thermally activated process and is followed by athermal growth. We suggest a composition-dependent expression for the activation energy of martensite nucleation upon quenching, which is used to predict whether the alloys retain the metastable beta phase at room temperature or transform into martensite. A model depending on composition, temperature and grain size, combined with empirical parameters, allows to describe the deformation behaviour of metastable beta alloys; the ones that display TRIP effect can be separated from those that display superelasticity or no stress-induced martensitic transformation. The method is assessed over more than 100 alloys reported in the literature. By being able to identify the composition-dependence of martensite formation upon quenching or via deformation, either reversibly or irreversibly, it becomes possible to design beta titanium alloys for tailored deformation behaviour.

Unsymmetrical functional isocyanurates

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Isocyanurates (or triazines-2-4-6-triones) are octupolar molecules that have attracted considerable attention in the field of polymer chemistry. However, until our recent investigations, only scant studies of the optical properties of isocyanurate derivatives have been reported. In this respect, we have shown that compounds such as three-substituted isocyanurates exhibit interesting two-photon absorption properties while being highly luminescent, which makes them promising for bioimaging and optical limiting applications.

To better understand the origin of these (nonlinear) optical properties, partially desymmetrized molecules without octupolar symmetry have been synthesized, and their photophysical properties have been studied and compared to those of the corresponding octupolar three-substituted compound.

Introduction to mineralomimetism: The photochromic property of hackmanite

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Photochromism can be defined as the reversible color change of a compound typically under ultraviolet illumination. Several gems are reported photochromic in the literature such as sodalite-hackmanite, scapolite-marialite, tugtupite and others. The ultimate goal of this study is to duplicate interesting behaviors or properties observed in natural minerals and optimize them for a potential industrial application. We call this mineralo-mimetism. If they are well defined and controlled, photochromic gem-inspired materials could replace organic ones with better (even infinite) cyclability and could lead to a new system for data storage for example.

Here we focus on hackmanite, the photochromic variety of sodalite ($Na_8Al_6Si_6O_{24}Cl_2$). This mineral presents a remarkable change of color from near-colorless to deep purple. The crystalline structure of this aluminosilicate contains “cages” holding $[Na_4]$ tetrahedrons with an anion at the center ($Cl^-, HO^-, CO_3^{2-}, SO_4^{2-}, \dots$). The substitution of this central anion is believed to induce the photochromism.

Namely, chemical and fluorescence analyses of natural stones (ICPMS-LA, XRF, XPS) do reveal the presence of noticeable amount of sulfur. This observation was the starting point of the aforementioned model : chloride (Cl^-) would be substituted by a S_2^{2-} (or more generally S_n^{2-}) ion. The excess of negative charge brought by S_2^{2-} replacing Cl^- would be hence compensated by a chlorine vacancy in an adjoining cage. Here, when irradiated by UV light, electrons of sulphur species are trapped in vacancies creating color centers responsible for the purple color. Once in the colored state, the reverse reaction occurs by irradiating the sample with visible light irradiation or by heating the sample. The photochromic reaction could then be written as : $S_2^{2-} + V_{Cl}^0 = S_2^- + V_{Cl}^-$

Whereas the model presented above is consistent with observations, formal justifications are rare, mainly because of the difficulty to analyze the sulphur species in such natural gems. That is why much work has been devoted to the synthesis of hackmanites. Today, synthesis of hackmanite is relatively easy.

Synthetic hackmanites have many advantages compared to naturals such as controlled composition and adaptable stoichiometry. Hence, chlorides in the cage can also be replaced by other halogens (Br, I). Substituting the halogen changes the color of the photo-generated state. So far we have analyzed natural and synthesic sodalites, mostly sulfur-doped. We already achieved similar kinetics of change between natural and synthetic samples by modifying the initial sulfate amount. XRD analysis confirms the sodalite structure of synthetic samples. Moreover, we recently initiated XPS analyses to try to prove which sulfur species are involved in the photochromism phenomenon. Our current researches aim to have an overview of all mechanisms involved in the photochromism of hackmanite. This, or these mechanisms could be extended to other related materials such as scapolite and tugtupite.

Combined NMR and X-ray diffraction study of structural aspects, dynamics and charge ordering mechanism in LixVOPO4.2H2O intercalation compounds

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Since the early 90s, with the use of the first lithium battery by Sony, the development of new positive cathode materials for lithium batteries has greatly increased in public and industrial research. Nowadays nearly 60 per cent of the batteries used are Li-ion type. Multiple families of materials were studied as lamellar structures (LiCoO2) widely used in the 90-2000s, spinel oxides (LiMnO4) and polyanionic frameworks including NASICON structures (AxMM'(XO4)3), Olivine (LiMPO4), Tavorite (AxM(XO4)Y)… These last structures are followed for their good network stability during the different cycles of the battery, a high energy density due to a high degree of oxidation of the transition metal used and a wide variety of elements that can be substituted for their synthesis. Despite many studies and the development of multiple positive electrode materials, the intercalation process of the alkali metal (Li, Na, K …) is not well understood[1].

We have been interested in the intercalation of lithium into the lamellar VOPO4.2H2O compound to obtain LixVOPO4.2H2O materials ($0 < x < 1$), studied by the combination of solid-state NMR and powder X-ray diffraction. In the present study, we aim at given preliminary results on the crystal structure and ageing of Li0.5VOPO4.2H2O.

Solid-state NMR experiments of 7Li were conducted in order to highlight Li preferential occupation sites, as well as the existence of dynamic exchange between different lithium sites on a time scale of the order of the millisecond for fresh samples. By combining these results with those obtained by powder X-ray diffraction, we observed a phenomenon of aging of the sample over several days.

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Hierarchical Electrode for High areal Energy on Chip Micro-Supercapacitors

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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 life-cycle 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 SiO2 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. SiO2 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 SiO2 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 SiO2 nanowires along the 100 µm-depth high aspect ratio structures. SiO2 nanowires have been synthesized by Rapid Thermal Annealing [3] (RTA) of SiO2/Pt thin films. In this study, we investigated manganese dioxide (MnO2) as electrode material. High specific area samples were firstly coated with a 50 nm-thick Pt layer which acts as a current collector and MnO2 seed layer. Then, MnO2 thin film was deposited by pulsed electrodeposition in 0.1M MnSO4 / 0.1M H2SO4 electrolyte to make a conformal deposition. First electrochemical measurements in liquid electrolyte (5M LiNO3) between 0 and 1 V vs Ag/AgCl of 3D electrode based on micro-tubes show a promising capacitance of 1 F.cm^{-2} at 2 mV.s^{-1} and 140 mF.cm^{-2} of a planar electrode based on SiO2 (NWs). By combining these nanostructured electrodes based on SiO2 NWs with 3D microstructures, the surface gains will be cumulated, to reach higher surface capacitance (>1500 mF.cm^{-2}).

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Measurement of an excess in the yield of J/ψ at very low p_T in Pb-Pb collisions at $\sqrt{s_{NN}} = 5.02$ TeV with ALICE

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In 2015, the ALICE collaboration reported the first excess in the yield of J/ψ at very low transverse momentum ($p_T < 0.3\ GeV/c$) in the forward rapidity region ($2.5 < y < 4$) in peripheral Pb-Pb collisions at $\sqrt{s_{NN}} = 2.76$ TeV at the CERN LHC. [1] The coherent photo-production is proposed as the potential underlying physics mechanism. This mechanism is the main responsible for low-p_T J/ψ production in ultra-peripheral collisions. However, the observation of a large effect also in more central collisions that are dominated by the hadronic interactions was quite surprising.

If the photo-production is confirmed as the origin of the excess, this will open up fundamental questions on the nature of the coherence in collisions where the nuclei break up. Furthermore, the J/ψ from the coherent photo-production could become a new probe of the Quark and Gluon Plasma. This poster presents the analysis strategy for Pb-Pb collisions at $\sqrt{s_{NN}} = 5.02$ TeV for which the data sample is expected to be about thirty times larger than at $\sqrt{s_{NN}} = 2.76$ TeV.

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A TD-DFT Study of Dual Fluorescence in Strap-ESIPT Systems

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Excited state intramolecular proton transfer (ESIPT) is a fast photo-tautomerization phenomenon occurring in the electronically excited state (ES) of a molecule exhibiting a strong intramolecular hydrogen bond. The emission from the ESIPT structure is strongly red-shifted compared to the absorption (large Stokes shift). Over the past few years, this phenomenon has been explored theoretically and experimentally to understand the detailed mechanisms taking place in ESIPT systems. The majority of the previously reported ESIPT dyes are characterized by a keto-enol tautomerism, in which the tautomerization is associated with a proton transfer along intramolecular hydrogen bond formed between two π-conjugated rings. An interesting class of ESIPT dyes was recently reported by Suzuki and coworkers [1]. This class encompasses compounds that have a dithienylpyrrole skeleton; the ESIPT system involving a strap moiety as the proton acceptor and a π-conjugated pyrrole scaffold as the proton donor. These compounds show a dual emission covering a wide range of the visible region depending on the solvent polarity. Considering the peculiar mechanism of ESIPT in this class of compounds, the red-shifted emission based on this ESIPT mechanism was explored in this work, by employing Time-Dependent Density functional theory (TD-DFT) calculations accounting for solvent effects with the Polarizable Continuum Model (PCM). A series of new substituted ESIPT chromophores, that have not been synthesized yet experimentally, were investigated in order to evaluate their fluorescence properties, as well as to understand their ESIPT mechanism by locating the transition state (TS). This provides insights into the impact of donating and accepting groups on the ESIPT efficiency.

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Speciation, solubility, and complexation of neptunium (V) under alpha radiolysis in carbonate media

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Currently, the most of electricity production in France (about 75%) is produced by nuclear which is based on the closed fuel cycle. The spent fuel from the cycle contains 96% of recoverable product such plutonium and uranium and 4% of not recoverable product as fission products and the minor actinides (neptunium, americium, curium...). The neptunium (Np) and others actinides are therefore considered as ultimate waste. These wastes are vitrified and stored in deep geologic (clay, granite, schist...) However, the presence of the radionuclides (Np, Am, Cm, ...) induces the phenomenon of radiolysis which leads to an alteration of the storage package which leads to the solubility of the neptunium. So, the latter can migrate into the environment.
Although, the chemistry of neptunium in carbonate media remains less studied than the uranium or plutonium, many authors have been reported previously that the studies spectrophotometric of the neptunium show many oxidation states (III, IV, V, VI and VIII)[1]. In environmental conditions, the most stable state is neptunyl ion (NpO_2^+) where the neptunium has an oxidation state +V. Indeed, in the presence of air and water, the Np (+III) will have tendency to oxidize whereas the Np(+IV) remains insoluble. As to the Np(+VI)is reduced easily in Np (+V) while the Np (+VII) is observed only in extreme conditions. The stability of Np (+V) allows having a great complexing affinity with hydroxyl and carbonate ions present in the water leading at the formation of many compounds such as $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, $NpO_2(CO_3)_3^{5-}$, $NpO_2(CO_3)_2OH^{4-}$, NpO_2OH over a range of pH ranging from 7 to 10 [2] [3]. These species have been characterized by visible UV with a characteristic band at 991 nm for $NpO_2CO_3^-$, at 998 nm for $NpO_2(CO_3)_2^{3-}$. However,$NpO_2(CO_3)_3^{5-}$ is not visible in wavelength range of 900 to 1100 nm [4]. These compounds are likely to be present during the alpha radiolysis of neptunium V in carbonate medium.
In order to follow the speciation of neptunium during radiolysis, a spectroelectrochemistry method was developed. The electrochemistry allows following the oxydo-reduction reactions likely to occur during the radiolysis. Many values of standard potential of $NpO_2^+/NpO_2^{2+}, NpO_2^+/Np^{4+}$ couples in absence of radiation have been reported in the literature [5]. Under the influence of the radiolysis, the water and carbonate break down into molecular and radical species ($HO^\bullet, H_2, H^\bullet, e_{a_q^-}, H_2O_2, HCO_2^-, C_2O_4^{2-}, CH_3CO_2^-...$). These species can be oxidant or reductive with regards to the neptunium present in solution and have effect on its oxidation state such as[6]:

$$2Np(VI) + H_2O_2 \rightarrow 2Np(V) + O_2 \tag{1}$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^- + HO^- \tag{2}$$

$$CO_3^- + Np(V) \rightarrow Np(VI) + CO_3^{2-} \tag{3}$$

The goal of this work is therefore to understand the influence of the phenomenon of radiolysis on the solubility of neptunium and potentially its migrations in an environment in carbonate conditions.

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Extended-TTF regioisomers: which impact for the corresponding self-assembled cages?

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Coordination driven self-assembly has allowed the preparation of a large variety of molecular macrocycles and cages. The corresponding host cavities offer promising molecular recognition properties, but very few of them are electro-active. On this ground, we have been interested in designing electron-rich self-assembled rings cages incorporating highly π-donating and S-rich frameworks, based on the so-called extended-TTF skeleton (exTTF, Figure 1). A key feature of this unit lies in a drastic change of the molecular shape upon oxidation. The latter evolves from a highly bent butterfly-like structure in the neutral state (exTTF) to a fully aromatic species (exTTF2+) where both 1,3-dithiole rings are separated by a planar anthracene moiety.

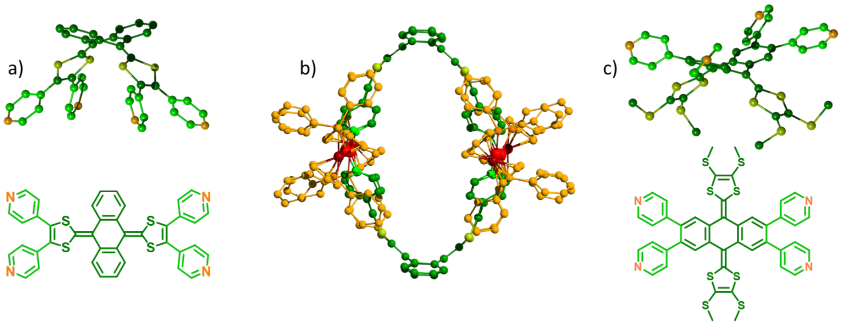

Figure 1 – X-Ray structures of (a) the butterfly-like exTTF ligand described in previous studies, (b) a corresponding self-assembled cage and (c) the isomeric exTTF' ligand discussed in this work, for which the four pyridyl units are linked to the anthracene moiety.

In this communication, we present our recent results in this field, related to the preparation of an isomeric ligand (exTTF') for which the four coordinating pyridyl units are now linked onto the anthracene moiety. The impact of this structural modification is studied in terms of i) comparing the electronic and geometrical properties of the corresponding cages and ii) of their relative binding abilities.

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Reactivity assessment of Passivated nanoscale Zero-valent iron

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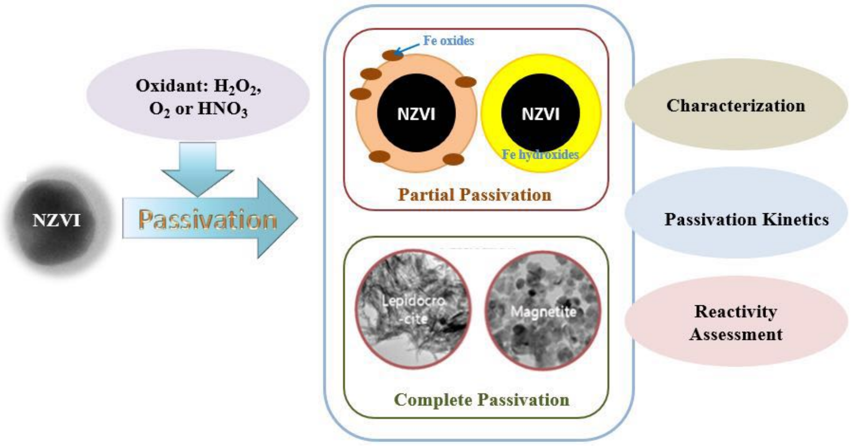
Nanoscale zerovalent iron (NZVI) has been considered as one of promising material in treatment of soil/groundwater/wastewater due to the potential advantages arising from high particle reactivity. It is commonly observed that NZVI undergoes surface oxidation (i.e., surface passivation) when it used for the removal of contaminants in variably oxic and anoxic environments. These processes often result in a decrease in NZVI reactivity. The aim of this study is to monitor the kinetics of NZVI passivation and identify the passivation byproducts that form with different oxidant. Three different oxidents, including H2O2, HNO3 and O2, were used to synthesis passivated NZVI particles. Characterizations such as. TEM, XRD were applied to identify passivation byproducts. Moreover, reactivity of these passivated NZVI particles were evaluated by sorption experiment under anaerobic conditions. In order to investigate comprehensive understanding NZVI passivated and how this passivation impact contaminant transport, pH and ORP during the whole process (including aging and sorption) were monitored.



Synthesis and characterization of redox active MOFs for positive electrodes batteries

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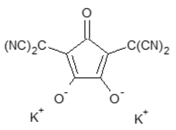
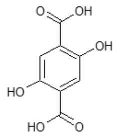
Currently, the field of Li-ion battery electrode materials is dominated by inorganic materials (oxides, phosphates), although organic materials have also recently re-emerged as promising alternatives. Hybrid organic-inorganic solids, in particular the porous ones, have been widely studied for various applications (gas capture or storage, catalysis)[1], but have been less studied for the electrochemical storage of energy. The organic-inorganic solids considered are crystalline coordination polymers (called MOFs, Metal Organic Frameworks) composed of inorganic entities (metal cation, cluster, chain) connected by organic ligands to define extended open networks. Both components have a great diversity of composition, leading to a huge variety of structure, porosity and eventually properties.

Few of these materials were shown to be suitable positive electrode material for Li-ion batteries, working as conventional insertion materials. These compounds, typically Fe or V carboxylates, oxalates and phosphonates operate on the $Fe^{(III/II)}$ or $V^{(V/IV/III)}$ redox couples[2,3,4], with their porosity promoting the diffusion of Li^+ ions concomitantly to the redox process. Nevertheless, their hybrid character is not exploited, as solely the inorganic part plays a role in the storage of charges . Our aim is to prepare solids which combine redox organic and inorganic activities, coupled with anion / cation insertion activities, allowing their use as electrode materials. In the literature, a few compounds such as $V^{IV}(Cl_4cat)_3{}^n$ (Cl_4cat = tétracholorocatécholate)[5] or $Fe^{III}{}_2(dhbq)^3(dhbq^{2-/3-}$ = 2,5-dioxidobenzoquinone/1,2-dioxido-4,5-semiquinone)[6] are presenting a hybrid redox activity.

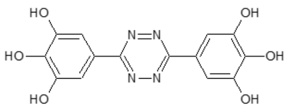
We focused our attention on small redox-active ligands carrying several complexing functions. Coupled with redox active metal cations (Fe, Mn, V), they should afford hybrid materials having a reasonable theoretical electrochemical storage capacity. Three redox-active ligands are currently studied:



Croconate violet (K_2CV)



2,5-dihydroxyterephtalic acid (H_2-BDC-$(OH)_2$)



s-tetrazinebisgallol (H_6-TzbisGallol)

In this communication, we will focus on the work carried out with the croconate violet. Several complexes built up from this ligand and electroactive cations will be presented. Their synthesis and structural characterization through a range of techniques will be presented, as well as their electrochemical behavior in the solid state.

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Penta(polyarene)fullerenes for pi-pi supramolecular assemblies

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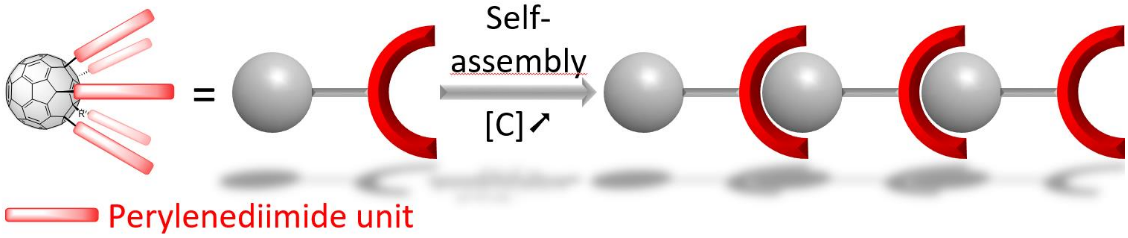
Thanks to its unique spherical structure and its strong withdrawing properties, fullerene C60 is a molecule of interest for electronic organic and supramolecular assembly. In this context, a variety of mono[1] and poly-fullerene[2] adducts have been described. Among them, penta-adducts developed by Nakamura and coworkers yield conical structures with a remarkable self-assembly capability.[3] Recently, the synthesis of a donor-acceptor supramolecular polymer based on penta(organo)[60]fullerenes bearing five electroactive fragments have been reported.[4] Here, we present the synthesis and studies of new supramolecular polymers based on penta(organo)[60]fullerenes bearing perylenediimide electroactive unit. The goal is to focus on pi-pi interactions. The self-assembly properties have been evaluated by NMR, cyclic voltammetry and atomic force microscopy.



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New Synthetic Methods for the Preparation of Saturated Heterocycles

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Five- and six-membered ring saturated heterocycles are key fragments that can be found in numerous compounds of natural sources, presenting potent biological activities. For instance tetrahydrofurans (THFs) and tetrahydropyrans (THPs) are recurrent motifs present in the skeleton of very complex compounds. The complexity of these structures is highlighted by the presence of substituents at the different possible positions of the ring and by the relative configuration of the stereogenic centres. Several efficient synthetic methods have been reported for the preparation of tetrahydrofurans[1] and tetrahydropyrans.[1a], [2] However, none of these reported methods are really general when both the substitution pattern and the relative configuration are taken into account and, as a result, the development of new synthetic strategies to access this important class of compounds from readily available starting materials is still highly relevant.

The project presented here aims at developing novel and efficient synthetic methodologies to provide access to polysubstituted-THP with good control of the stereocentres. Our recent results in this field will be discussed.

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Molecular Dynamics simulations of rare-earth-doped nanoparticles in silica matrix: drawing of a preform to a fiber

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The encapsulation of luminescent ions in dielectrics nanoparticles embedded in vitreous silica is a promising strategy to tailor the spectroscopic response of rare-earth-doped silica fibers. Previous studies have shown an improvement of the spectroscopic properties[1,2] and a decrease of the rare-earth clustering effect[3] when Er^{3+} ions are embedded in Mg-silicate nanoparticles compared to a pure silica matrix. By means of molecular dynamics simulations, nanoparticles are formed in situ through phase separation mechanism within MgO-SiO_2 binary melt using an adaptative interatomic potential[4]. The simulated preforms are doped with Eu^{3+} and Er^{3+} ions, and are then deformed into a fiber while glass flow effects (thermodynamical and rheological) leads to modifications of the nanoparticles morphology. In this study, we highlight a rare-earth encapsulation in Mg-silicate nanoparticles more efficient for Er^{3+} ions than for Eu^{3+} ions. Moreover, the MgO concentration seems to converge toward a maximum value when the nanoparticles grow. Finally, preliminary results concerning the influence of the drawing parameters (temperature, elongation velocity) on the sizes distribution and on the morphology of the nanoparticles are also presented.

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Equation of state of the matter at finite temperature and finite chemical potential using the PNJl model

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We present an equation of state of the matter at finite temperature and finite chemical potential using the PNJl model. The equation of state goes to the next to leading order $O(\frac{1}{N_c})$ including mesons participating to the pressure of the medium below T_c. Together with a new parametrisation of the effective Polyakov loop involving the presence of quarks in the determination of the critical temperature, we determine a pressure at zero chemical potential matching the result of the lattice and expand to finite chemical potential. Also derivatives as the entropy density, energy density, measured interaction and speed of sound are very similar to lattice results at zero chemical potential and can be expanded to finite chemical potential. Regarding the finite chemical potential, the Taylor expansion around zero chemical potential also match the results of the lattice. This new equation of state allows for neutron star calculations.

Synthèse et caractérisation avec spectroélectrochimie de catalyseurs à base de métaux de transition pour l' électroréduction au CO_2

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Au cours des dernières années, des progrès significatifs ont été réalisés dans le domaine de la réduction électrocatalytique du CO_2 par des complexes métalliques (Ni, Mn, Fe, . . .). [1,2] Tout particulièrement, les complexes de molybdène et de tungstène carbonyle porteurs d'un ligand bipyridine ont attiré l'attention.[3] Dans ce contexte, nous avons développé de nouveaux complexes $[Mo(CO)_4(bpy\text{-}R_2)]$ (R = H, tBu, OMe, CO_2H), en concentrant nos efforts sur la modulation des propriétés électroniques du système par variation du substituant R sur le motif pyridine. D'autres systèmes présentant des ligands non-innocents d'un point de vue redox, tels que $[Mo(CO)_4(phen)]$ et $[Mo(CO)_4(dpa)]$ sont également à l'étude. L'objectif de ce travail est d'obtenir de nouveaux électrocatalyseurs et de corréler les résultats électrochimiques et spectroscopiques à des résultats DFT afin de mieux comprendre le mécanisme de la catalyse par ces systèmes.

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Structural and electronic response of materials under intense THz light

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In condensed matter physics, phase transitions is an important field of research. By adjusting the control parameter, matter can switch from one state to another. Usually those are temperature or pressure, however magnetic field, electric field or even light can be used as a control parameter. Visible light has been successfully used as a control parameter for many years [2]. Nevertheless, the energy of the fundamental modes, including phonons or motion of free electron are several order of magnitude lower than the energy of visible light, matter needs to dissipate the energy by adding heat to the system. Hence, the need of a low energetic light : the THz light. Also, the pulse duration of THz light allows very important electric field up to 1MV/cm [1]. Such a field allow to study electric response with a complete new angle. In this poster, the generation of a THz light source and a compound presenting multiple type of response to THz field will be presented.
THz light was successfully generated using optical rectification within the $LiNbO_3$ non linear crystal. This crystal presents the best performance for this method however one need to add the tilted pulse front technique in order to achieve the most intense THz field from it. [1]
The $Fe(phen)_2(NCS)_2$ or fephen is a spin crossover molecule. Fephen is a butterfly like molecule, the central atom is Fe^{2+} and the two legs are $(NCS)^-$ which implies a dipolar momentum within the molecule. Structural modification accompanies the spin crossover transition, hence by driving breathing mode of the molecule with THz light, we could induce a change of the spin of the Iron. The intense electric field of THz light would also allow us to act on the dipolar momentum of the fephen crystal and induce ferroelectricity at a macroscopic scale. Simulations, which will be presented here, are presenting promissing results for both aspects.

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Analysis of distortions during Wire Arc Additive Manufacturing (WAAM)

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Although the additive manufacturing, i.e. 3D forming process by adding material layer upon layer, was born in the 19th century, it gained interest for only three decades. Currently, powder feed additive manufacturing technologies have reached a certain limit, that's why developing Wire Arc Additive Manufacturing (WAAM) processes appears to be necessary. Indeed, WAAM provides the advantage of generating large size components at a lower cost than with powder feed systems. However, to this day, WAAM does not lead to parts as thin, accurate and flawless than powder techniques.

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

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

It aims :

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

The final purpose of this study is to conduct to the development of an equivalent numerical model coupling thermal, mechanical and metallurgical aspects of the WAAM process which should give the possibility to forecast defects, distortions and residual stresses and thus to design sustainable pieces.

Calibration of the SoLid detector

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The SoLid experiment, at SCK • CEN BR2 research reactor in Belgium, will address one of the most issue in neutrino physics: the experimental neutrino flux anomalies, called Reactor Antineutrino Anomaly (RAA), that are pointing towards the existence of a new neutrino state with a mass of around 1 eV. Moreover a measurement of anti-neutrino energy spectrum produced by ^{235}U which will help on 5-MeV distortion seen in the neutrino-reactor-experiment data.

The SoLid technology is based on a novel approach combining PVT cubes of 5×5×5 cm3 and 6LiF:ZnS (sheets $\approx 250\ \mu$m thickness) scintillators which allows us to have a good discrimination between electromagnetic and nuclear signals. The system is read out by a network of wavelength shifting fibres and MPPCs and allows a precise localisation of the IBD products.

The high segmentation represents a challenge to achieve calibration requirements needed for SoLid scientific goals. In each detection volume (12.800 cubes), a good control of the neutron capture efficiency and of the energy scale is necessary. The latter must be known with a precision better than 2%. For that we used several neutron and gamma sources such as: AmBe and ^{22}Na. This poster will present methods used by the collaboration to measure neutron capture efficiency and also Compton edges for linearity and energy scale purposes.

Electrical characterization of new polymer: fullerene blend thin films used in solar cells

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This paper presents the study of thin films based on polymers with different weight ratios of fullerenes leading to an individual characterization of two distinct polymers, as well as adding the fullerenes. The novelty is the introduction in individual study of a new polymer [1,2] poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b'] dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c'] dithiophene-4,8-dione)], known as PBDB−T−SF or PCE13, working in comparison with poly (3-hexylthiophene-2,5-diyl) (P3HT). Its peculiar feature, the presence of two atoms of fluorine in polymer backbone, represents an advantage because of the electron-withdrawing effect, avoiding also the steric hindrance of inter- and intramolecular systems. This fact may enhance the crystallinity and may facilitate the charge transport.

The study is involving three sets of samples deposed by spin coating on indium tin oxide (ITO) substrates: set 1 − P3HT and PBDB−T−SF thin films (90 nm thickness) from chlorobenzene solution (12.5 mg/mL and 10 mg/mL); set 2 − P3HT:PCBM (1:0.8) and PBDB−T−SF:PCBM (1:1) blend thin films (90 nm and 130nm thickness) from chlorobenzene solution (10 mg/mL) adding 1,8-diiodooctane (DIO); set 3 − P3HT:PCBM (1:0.8) and PBDB−T−SF:PCBM (1:1) blend films (200 nm and 300 nm thickness) from chlorobenzene solution (16 mg/mL and 14 mg/mL) adding 1,8-diiodooctane (DIO). From the optical point of view, PBDB−T−SF is a better optical absorbent than P3HT, increasing this property with the increasing of the fullerenes, PCBM. An optical shift is well shaped on the optical parameters (by ellipsometry – refractive index and extinction coefficient). These results were corelated with the morphological and the electrical properties. From electrical conductivity characterisation, during several heating and cooling cycles (between 30 and 120°C), it results that P3HT is more conductive than PBDB−T−SF, but, a visible change in conductivity values occurred after PCBM addition. The decrease of the resistance in the case of blends is more pronounced in case of PBDB−T−SF where the decreasing is of almost 10 times comparing to P3HT for witch only few kΩ decreasing in resistivity was observed, however the electrical conductivity of P3HT:PCBM blend is much important than of PBDB−T−SF:PCBM blend.

In a brief conclusion, this paper brings additions and novelties on the properties and behaviour of polymers, highlighting the properties of PBDB−T−SF for its future applications in solar cells.

Haluminogen effect: Playing with Halogen atoms for activating mechanoresponsive luminescence in pure organic materials

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Emissive pure organic solids with desirable colour emission and high efficiency are the target of much interest because of their potential applications in optoelectronic devices such as organic light-emitting diodes or solid-state laser[1]. Recently it has been demonstrated that the emission colour and the emissive efficiency in the solid state of pi-conjugated materials are not only due to the conjugated molecular structure but are decided by the intermolecular interactions between neighbouring molecules[2]. Mechanofluorochromic materials presenting colour emission changes via a modification of the molecular assembled structures through mechanical stimulation are emerging[3].
In the present work, we have developed new luminogen derivatives Ia-c, associating halogen atoms and furan cycle, that present an Aggregation Induced Emission (AIE) effect[4] (Figure 1).
We show that the halogen atoms induce also mechanoresponsive luminescence characteristics, allowing us to define compounds Ia-c as haluminogen materials.

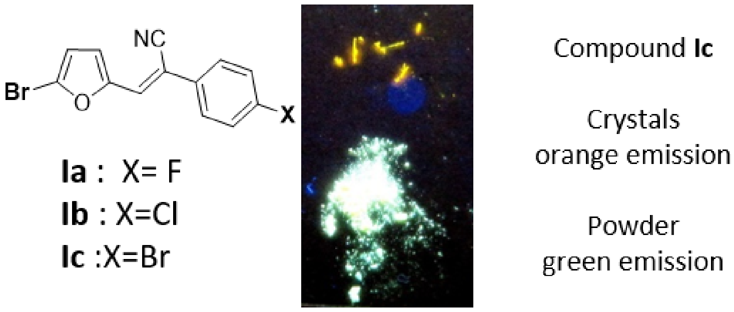

Figure 1 – Molecular structure of compounds Ia-c. Colour emission of compound Ic under irradiation at 350 nm for the powder or the crystals

The influence of the halogen atoms on the photophysical properties in relation with the crystalline phases obtained from the X-ray diffractions measurements will be presented and discussed.

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Green-synthesis of anisotropic gold nanoparticles for *Surface Enhanced Raman Spectroscopy* and bio-applications

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Gold nanoparticles (Au-NPs) present low toxicity and remarkable optical and electronic properties, so their integration in biological systems could prove very useful, either as a probe for imaging or as a drug carrier for medical therapy applications[1]. The anisotropic nanoparticles synthesis methods often include toxic surfactants like CTAB (Cetyl trimethylammonium bromide) that has to be eliminated before their application in biological environment. Alternative methods consist in using plant extracts as reducing agents[2,3]. In this work, we present the biosynthesis of Au-NPs using Aloe Vera leaf extract. In a first set of experiments, the concentration of reducing agents is modified and the distributions in size, shape, crystalline structure and quantity of Au-NPs are systematically analyzed using transmission and scanning electron microscopy and atomic force microscopy. In a second phase, the impact of the synthesis duration on the particles size and shape has been studied. Finally, UV-vis-NIR absorption spectroscopy measurements have been performed, highlighting the plasmonic properties of the nanoparticles. Surface Enhanced Raman Spectroscopy (SERS) measurements are under investigation.

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Chemically modified recombinant adeno-associated vectors for specific delivery of a gene of interest

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Adeno-associated viral vectors (AAV) are highly efficient tools for the transfer of therapeutic genes into target cells[1]. It has been shown to be effective for the treatment of genetic diseases and more than one hundred clinical trials using AAV are in progress. Those clinical trials led to the commercialization of two drugs, Glybera and Luxturna. However, despite clinical advances and the commercialization of treatments[2], the use of AAV remains a challenge and some limitations have been observed. For example, AAV possess a wide tropism and can be distributed to off-target cells and AAV can also be neutralized by circulation antibodies in patients, thus, preventing efficacy of the treatment. The present project aims to develop novel AAV vectors coupled to a chemical molecule to increase the target efficacy. First, we selected a ligand that specifically recognize the target cell and then the ligand is coupled to the AAV capsid by a defined reactive function thanks to a click chemistry reaction. This function will allow the bioconjugation of the ligand on the virus to obtain an AAV chemically modified and achieve a better therapeutic index. During my PhD, I have synthesized several chemical compounds with the reactive function. Next, it will be necessary to couple the ligands to the AAV and demonstrate a covalent coupling. Finally, we will study of the biological properties of the chemically modified vector to transduce the target cells in primary culture and upon in vivo administration in animal models.

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Sorption and Redox Reactions at the Mn-oxide/Water Interface

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The manganese (Mn) bearing minerals are abundant in the environment, and can play a major role in the migration and transformation of contaminants in soils and groundwater.[1,2] The Mn-oxides with layer structures exhibit the negative structural charge caused by Mn site vacancies and the substitution of Mn(IV) by lower valence cations. Mn(III) ions can bind to vacant sites and be incorporated into those sites of birnessite, which can further influence the properties of Mn-oxides.[3] In addition, Mn-average oxidation state (AOS) may impact the reactivity at oxide/water interfaces, and then sorption and redox reactions with Mn surface sites.

In this research, two birnessites (layered structure), acid birnessite and $\mathrm{Mn}^{\mathrm{III}}$-rich birnessite were synthesized and characterized by X-ray powder diffraction, energy-filtered transmission electron microscopy, X-ray photoelectron spectroscopy and vibrational spectroscopy. The reactivity against different kinds of compounds was assessed using high performance liquid chromatography mass spectrometry (HPLC/MS) and UV-Vis spectrophotometry under different experimental conditions, including pH, ionic strength and presence of natural organic matter (NOM). The AOS of the Mn-oxides were also measured through oxalic acid-permanganate back titration method to evaluate the correlation between AOS, binding capacity and surface charge.

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Studies of ion-molecule reactions at low temperatures using a mass selective plasma source coupled with a uniform supersonic jet

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Ions are detected in trace amounts in astrophysical environment like interstellar clouds and star forming regions to protoplanetary disks and circumstellar envelopes. A new approach based on the uniform supersonic flow technique - a cold, thermalized de Laval expansion offering the advantage of performing experiments with condensable species - has been developed to study ion-molecule reactions at low temperatures down to 15 K. Ions are produced by discharge (pressure $\sim$ 0,1-10 mbar). This technique employs a mass-selective radio frequency transfer line to capture and select ions from an adaptable ionization source and to inject the selected ions in the core of the supersonic expansion where they are monitored by a movable mass spectrometer along the axis, the reaction rate k of the selected ions with the neutral molecules present in the flow is derived by examining the ion evolution vs. distance from the nozzle (equivalent to reaction time). We poster present the new experimental setup, and some results obtained recently using CRESU-SIS (technique CRESU with new mass selected ion source) .

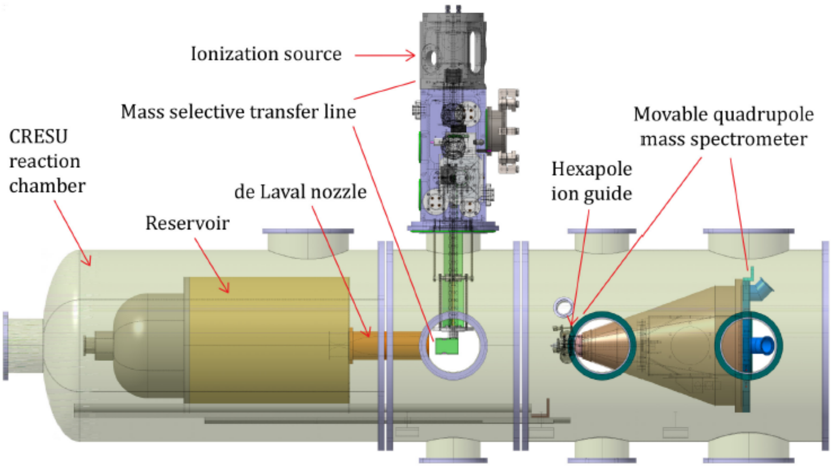

Figure 1 – Experimental setup

Non-destructive analysis: PIXE with high-energy ion beam analysis at the ARRONAX cyclotron

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Particle Induced X-ray Emission (PIXE) with high-energy ion beam analysis performs a non-destructive multi-element analysis. This analysis allows the identification and quantification of medium and heavy elements in the samples, with a resolution of μg/g [1, 2]. Several studies have shown the interest of coupling this method with another using gamma rays (Particle Induced Gamma Emission - PIGE) to analyze light elements [2, 3]. In order to perform the PIXE analysis, it is necessary to know lots of important information: the fundamentals parameters like the K shell ionization cross section, and the experimental parameters such as the detector efficiency and the intensity of the ion beam. In this study, Several methods, based on different available detectors (X-ray detector, photomultiplier for UV-visible, ionization chamber), for the measurement of the beam intensity, were characterized for different ions (protons, deuterons, alpha particles) at different energies (17 to 68 MeV) and for a wide range of intensity (150 fA, 40 nA). The results show the optimal ranges of use of each detector according to the experiment requirements in terms of energies and intensities of the delivered beam. Another part of the study was devoted to determine the characteristics of a semiconductor x-ray detector (XPIPS) using by PIXE experiment. A X-ray microtomography was used to determine the thicknesses of the vacuum layer and the Si semiconductor layer. The comparison of the theoretical model of the detector efficiency with the experimental measurements, realized with the Fe-55 (5.9 keV) and Cd-109 (22.1 keV) X-ray sources, as well as the gamma-rays source Am -241 (59.5 keV), allowed to determine the thicknesses of the window Be and the active layer of the detector. Finally, different measurements of production cross sections, with proton energies were made for different targets (Ag, Au, Cu and Ti).These results could be compared with existing data and a theoretical model [3].

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Functional Luminescent Cu(I) Polymetallic Supramolecular Assemblies

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Cu(I) complexes have received increasing attention because copper is a relatively inexpensive and abundant non-noble metal, and the d10 electronic configuration in Cu(I) ion can yield intense photoluminescence properties. Recently, many Cu(I) complexes exhibiting thermally activated delayed fluorescence (TADF) have been developed, and some are promising candidates for use in highly efficient, lighting and sensors applications. In our group, we have synthesized a new series of luminescent Cu(I) polymetallic assemblies obtained using a supramolecular Cu4 metallacycle A precursor. These compounds could present original luminescence properties (thermochromomism, vapochromomism and mechanochromism). Their syntheses, solid state characterization and photophysical properties will be described in this poster.

Perspective for a very fast radiolabeling pathway of new Astatine compounds and comparison studies in different media

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Astatine is the rarest natural element in the earth's crust. It is a radioelement whose isotopes have a half-life of several hours. Astatine-211 is a very promising radioisotope for nuclear medicine and can be produced in cyclotron via the reaction (1).

$$^{209}_{83}\mathrm{Bi} + ^{4}_{2}\mathrm{He} \rightarrow ^{211}_{85}\mathrm{At} + ^{2}_{0}\mathrm{n} \qquad (4)$$

Being a halogen and a 100 pourcent alpha emitter makes him one of the best candidates for targeted alpha therapy. However, the radiolabelled molecules currently being developed show some limitation, i.e. carbon-astatine bond undergoes deastatination after internalization in cells[1]. To overcome this problem, a boron-astatine bond instead of the conventional organic carbon-astatine bond was proposed using boron clusters [2]. These compounds give good stability results [3], thanks to the stronger boron-astatine bond than the carbon-astatine bond [4][5]. However, the distribution of antibodies depends on the linker and the nature of the boron cluster and counterion used for the boron cluster[3;6]. At SUBATECH, with the collaboration of CEISAM and CRCINA, in Nantes, we have developed a new compound that is highly reactive with astatine, using iodonium salts as a precursor. These precursors are being developed at CRCINA for radiolabelling of astatine [7]. With this new compound, we have quantitative labelling at room temperature in just a few minutes. These results break with the previous efficacy of any other organic compound forming carbon-astatine bonds. We are currently studying the stability of the labelling under conditions of interest: phosphate buffered saline solution, physiological serum and in oxidizing conditions following the recent work of D. Tezé et al. [8]. The stability is compared to a labelled molecule representing the one currently used, i.e. the SAB (N-succinimidyl 3-astatobenzoate). Before stability tests, a purification process of the labelled molecule is followed to ensure good chemical, radiochemical and radionucleidic purity. The stability is followed either by HPLC or by Thin-layer chromatography (TLC) using gamma or UV detection for At-211 and the chemical products, respectively. The results currently being finalised will be presented.

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The interplay of phases, structural disorders and electric behaviors in Al doped $BiFeO_3 - BaTiO_3$ ceramics

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Al doped $BiFeO_3 - BaTiO_3$ (BFA-BT) systems with a defined composition were prepared by solid-state method. The enhanced spontaneous and remnant polarization were achieved in $BiFe_{0.970}Al_{0.030} - BaTiO_3$ with 36.8 $\mu C/cm^2$, 31.5 $\mu C/cm^2$ respectively. For SEM and XRD analyses, the high-density microstructures and the high c_T/a_T as well as high distortions of the rhombohedral phase were found to play the dominant role in the enhanced piezoelectric properties. High polarization and strain were achieved in the $BF_{0.970}A_{0.030} - BT$ system. ^{57}Fe Mössbauer spectra revealed the large disorder of Fe^{3+} at B sites preferentially occupied by more Al^{3+} doping ions, forming the diffusive phase transition for dielectric behaviors in samples. Grain and grain-boundary effects were pointed out from the dielectric modulus and a related thermal evolution. AC capacitances indicated two relaxation processes marked by the grains and interfaces involved in the polycrystalline ceramics for highly doped systems. The work will be significant to illuminate the interplay between structures and properties in ferroelectric materials.

Formation of ultrathin layers exploiting dioxygen reduction for diazonium electrografting

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The surface functionalization with covalently attached films is of increasing interest for modifying the surface properties of various substrates. One of the most used approach is the grafting of aryldiazonium salts by electroreduction.[1] The electroreduction of diazonium salts produces aryl radicals, which anchor to the surface forming a covalent bond. These radicals are higly reactive species and attack the already immobilized molecules leading to the formation of multilayer. Several strategies including for example the use of diazonium salts containing bulky substituents[2] have been developed to prevent the radical attack on immobilized molecules and to provide controlled films with better sensitivity and reactivity on the surface.

Here, we report a strategy [3] to form organic monolayers on carbon surface by exploiting the reductive properties of superoxide ions at the grafting potential to control the radical polymerization. The dioxygen is reduced (Figure 1) at the electrode and the formed superoxide ions diffuse to react with the approaching diazonium to limit radical attack.

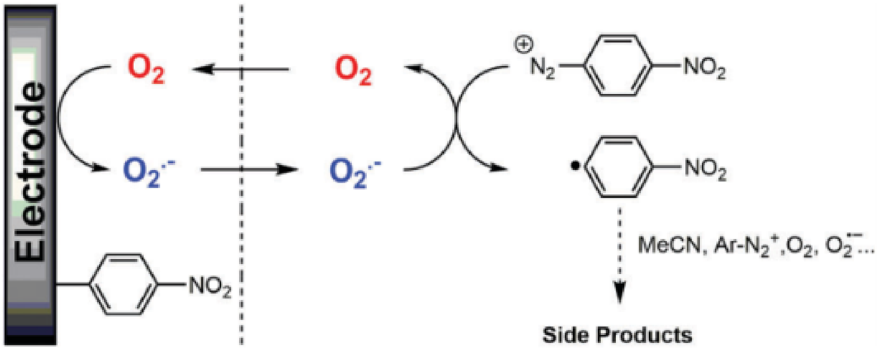

Figure 1 – Redox catalytic process involved in diazonium electrografting

This technique leads to the formation of ultrathin films without any specific synthesis or redox mediator addition. The obtained monolayers were probed by cyclic voltammetry, impedance spectroscopy, X-Ray photoelectron spectroscopy and atomic force spectroscopy.

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An in vitro system to assess the enzymatic dephosphorylation of phytate during digestion process of different materials

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Phytate, the perphosphorylated myo-inositol, is the main source of organic phosphorus in cereals, beans and legumes. Phosphorus from this compound is poorly available for livestock and is thereby excreted and accumulates in soil with various harmful environmental effects. Moreover, this molecule has also various antinutritional properties, such as the reduction of other nutrients' availability (cations, proteins. . .) due to complexes' formation. To overcome these issues, phytases are used as additive in animal nutrition in order to help the hydrolysis of phytates during the digestion process. In vivo studies have shown an influence of the diet's composition on phytase benefits, but these in vivo investigations are complicated, expensive and difficult to rationalize. Then, in vitro simulations represent a major alternative for the investigation of phytase properties.

A three-step in vitro digestion model was set up. Temperature, pH, proteolytic enzymes, and incubation time were adapted to simulate the conditions in the crop, stomach and small intestine of poultry. Various amounts of exogenous phytases were added to the different matrices (grounded wheat, maize, soybean meal, rapeseed meal, sunflower meal and rice bran) and final contents of inositol phosphates (IP6 to IP3) were measured by HPLC.

With a phytase concentration of 500U/kg, a common concentration in feed products complemented with phytases, very different results were obtained depending on the matrix: from a 91% reduction of the initial amount of phytic phosphorus in wheat to only 20% in rice bran. The inorganic phosphorus released during the simulation was also very different, ranging from 1.0 (maize) to 3.3g/kg (soybean meal). This in vitro digestion system has shown its potential to evaluate the diet composition influence on phytase activity. The two aspects of phytases benefits are monitored: the antinutritional compound degradation and the phosphorus availability increase. These results have now to be correlated to in vivo studies.

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First evidences of the flexoelectric responses of PEDOT-PSS polymers

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The project concerns the field of electroactive polymer films intended to ensure a mechanical to electrical energy conversion. The transduction mechanism considered is the flexoelectric effect, which corresponds to the appearance of an electric polarization induced by a deformation gradient (equal to the curvature) This effect that is different from piezoelectricity is present in all the dielectric (insulator) solids [1]. However, a recent study [2] about flexoelectric effect in oxide thin films revealed a three orders of magnitude enhancement of the effective flexoelectric coefficient accompanied by a large increase in the dielectric constant, after the insulating oxide has been reduced to a semi-conducting sample. Thus, the main objective of the present study is to explore the flexoelectric responses of organic (semi)-conductor films. As a first step films of poly (3, 4-ethylenedioxythiophene- poly (styrene sulfonate) (PEDOT-PSS) have been studied. PEDOT-PSS is a classical conducting polymer used in the elaboration of optoelectronic devices [3].

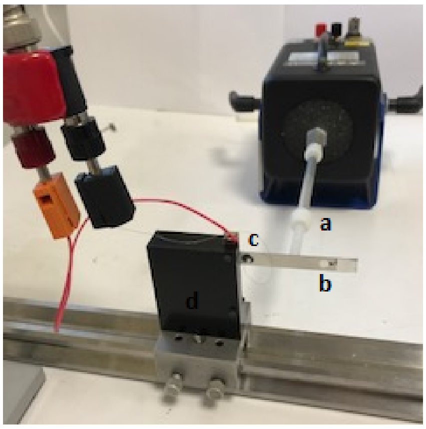

Figure 1 – Schematic of the lab experimental setup: a. vibrator, b. stainless steel substrate, c. film with Al top electrode and metallic wire, d. sample holder.

In this way, various commercially available PEDOT-PSS polymer solutions have been deposited by drop casting on stainless steel substrates with different volumes leading to varied polymer thicknesses (µm range). Polymer films were covered with aluminum top electrodes up to 100 nm in thickness using a metal evaporator) and the complex permittivity and conductivity were measured to possibly establish a correlation with the flexoelectric coefficient. This latter has been obtained by current output and deflections measurements of bending cantilever-shaped samples using the lab setup showed in fig.1.

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Interlocked Donor-Acceptor Cages: an innovative supramolecular approach to organize active materials for solar cells

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One of the main challenges in the field of organic photovoltaics (OPV) lies in the control of the morphology of the photoactive layer, constituted by electron donor (D) and acceptor (A) patterns. In this context, we wish to develop interlocked donor-acceptor cages, in order to control the organization of these D and A patterns. In particular, supramolecular coordination cages built by self-assemblies driven by metals are very good candidates because of their easy way to synthetize and their ability to self-assembly spontaneously, to constitute interlocked three-dimensional structures [1]. Self-assembled coordination cages are obtained by spontaneous association between polytopic ligands, with symmetry C3 in our case, and metallic complexes with a pre-organized geometry. In the context of our current works in the lab to produce self-assembled molecular receptors [2], we recently observed a ligand based on truxene core, associated with dinuclear Ruthenium complexes can produce interlocked cages. Indeed, by assembling a truxene ligand functionalized by three butyl chains and a dinuclear ruthenium complex, spaced by a naphto pattern, we were able to obtain an interlocked cage.

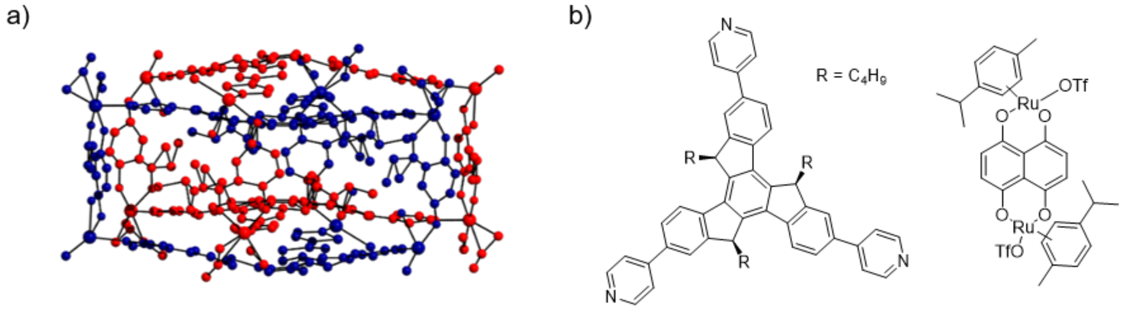

Figure 1 – a) RX Structure of the interlocked self-assembled cage based on truxene core, b) Truxene ligands and ruthenium complex

On the basis of this result, we wish to prepare a new family of polycatenanes of interlocked coordination cages, involving for each of them partners D and A, using as donor the triazatruxene fragment (D), which has the same symmetry than the truxene and more electron donor, associated with dinuclear acceptors of ruthenium (A) in order to produce the first OPV cells based on coordination cage.

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Organocatalyzed Ring-opening polymerization of substituted β-lactones: Investigation of the Mechanism and PHAs structure by MALDI-TOF mass spectrometry

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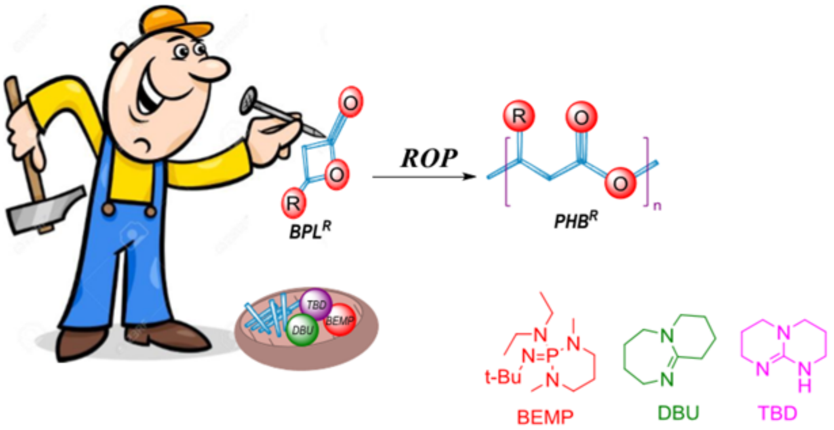
To date, polyesters, both natural and synthetic, constitute the most fully developed class of degradable polymers. The organocatalyzed ring-opening polymerization (ROP) of 4-alkoxymethylene-β-propiolactones "BPL$^{\mathrm{OR}}$s" towards the formation of the corresponding polyhydroxyalkanoates "PBPL$^{\mathrm{OR}}$s" was investigated using basic organocatalysts of the guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD), amidine (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU), and phosphazene (2- tert -butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine, BEMP) type. Insights into the polymerization mechanism was gained through detailed 1D/ 2D NMR spectroscopy and MALDI-ToF/ ESI MS analyses of the resulting "PBPL$^{\mathrm{OR}}$s" and in particular of the end-capping groups.



Synthesis of Phenanthroselenophenes via Pd-Catalyzed Successive C–H Bond Arylation and Annulation

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Planar π-extended organic molecules are considered the next generation of electron-transporting materials for opto-electronic devices. [1] Several analogues containing an heteroaromatic unit such as thiophene, or pyrrole have been synthetized and have found number of applications as electronic components for the preparation of devices. [2] Despite the recent interest of selenophenes as building blocks of organic materials [3] useful for the construction of optoelectronic devices, only scarce examples of planar π-extended containing selenophenes have been prepared in the literature. [4]

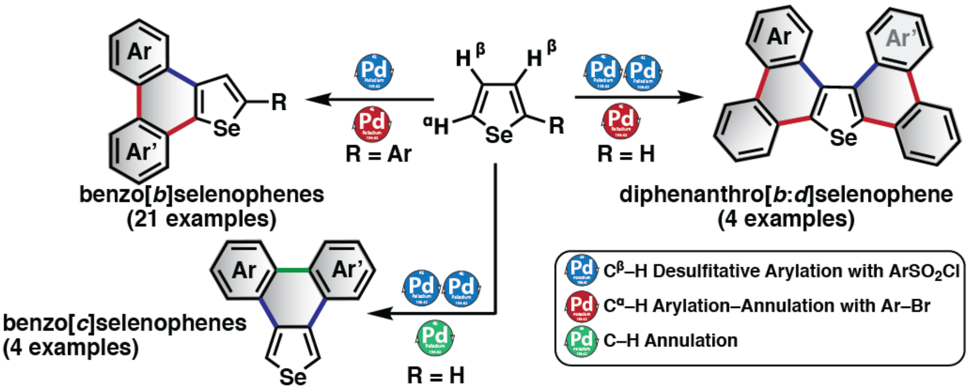

Figure 1 – Synthesis of Phenanthroselenophenes via Pd-Catalyzed Successive C–H Bond Arylation and Annulation.

In this goal, we have achieved the synthesis of a wide diversity of well-decorated π-extended aromatics containing selenium atom from selenophene using the combination of three to six C–H bond arylations. The key step was the introduction of (2-bromo)aryl group(s) at β-position of selenophenes using Pd-catalyzed desulfitative arylation with (2-bromo)arylsulfonyl chorides. Then, Pd-catalyzed one-pot tandem C–H direct arylations of selenophene rings at α-position with aryl bromides followed by annulation reactions afforded phenanthro[b]selenophenes. In contrast, using a second Pd-catalyzed desulfitative arylation at β'-position of selenophenenes followed by a cyclization reaction, phenanthro[c]selenophenes were obtained. Rapid construction to exotic scaffolds such as diphenanthro[b:d]selenophenes has also been achieved by double Pd-catalyzed α-arylation – annulation reaction. (Figure 1).

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Innovative approaches in drug discovery : *Inhibitors of Protein-Protein Interaction for RhoGTPases*

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La superfamille des protéines Ras est constituée de 5 sous-familles dont les protéines Rho (Ras homologous) qui comportent 20 membres chez l'Homme. Au sein de cette sous-famille, les protéines Rac1, RhoA et Cdc42 sont les plus étudiées. Elles sont impliquées respectivement dans la formation de lamellipodes, de fibres de stress et de filopodes en ayant des conséquences sur la morphologie, la polarité, la contraction, la motilité et l'adhésion cellulaire.

Les protéines Rho sont des GTPases de petites tailles (20-25 kDa) qui présentent des structures caractéristiques de la famille Ras avec 6 feuillets β et 5 hélices α. Entre chacun de ces feuillets et de ces hélices, il y a 5 boucles notées de G1 à G5.1 (Fig. 1). Ces boucles vont permettre les interactions avec le GTP (Guanosine Tri-Phosphate) ou le GDP (Guanosine Di-Phosphate) et le cation Mg^{2+}. Ces protéines sont considérées comme des interrupteurs moléculaires (« switch ») pouvant passer d'un état inactif lié au GDP à un état actif lié au GTP pour permettre la mise en jeu de voies de signalisation intracellulaires. [1]

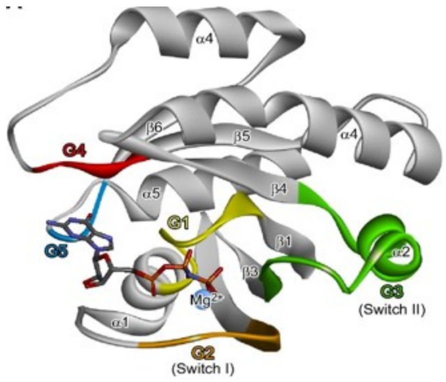

Figure 1 – Structure typique d'une protéine Ras avec l'exemple H-Ras impliquée dans un complexe GTP.

Les protéines RhoA et Rac1 sont toutes deux impliquées dans la contraction des cellules musculaires lisses vasculaires et bronchiques. Elles sont respectivement reconnues pour leur rôle dans l'hypertension artérielle [2] et l'hyperréactivité bronchique associée à l'asthme. [3]

Depuis de nombreuses années, le nombre de molécules obtenant une autorisation de mise sur le marché stagne malgré les fonds financiers importants engagés par les entreprises pharmaceutiques. Il semble évident que les stratégies de découverte de médicaments méritent un ajustement, un renouveau. Dans ce contexte, les interactions protéine-protéine sont un choix stratégique pour un nouveau ciblage thérapeutique. [4]

Dans le cadre du projet PIRAMID[5], nos travaux portent sur la découverte de molécules ciblant les interactions des protéines Rac1 et RhoA avec leurs partenaires. Nos molécules cibles visent à bloquer le passage des protéines inactives lié au GDP à l'état actif lié au GTP.

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[5] http://piramid-research.fr/

Modelling of High-power impulse magnetron sputtering under Ar/O2 mixture using global kinetic model

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The high power impulse magnetron sputtering (HiPIMS) discharge is a recent addition to plasma based sputtering technology, it has been successfully introduced into various industrial and technological applications especially in semiconductor manufacturing. The use of a HiPIMS power supply represents an alternative to DC or RF Physical Vapour Deposition (PVD) processes. It can produce high plasma densities of the order 10^{19} $m{-}3$, and get highly ionized metal plasmas. Differently than the other mid-frequency regime (5-350 kHz), theses discharges can work at a very low frequency mode with long “off” times, and they provide short duty cycles but ultra-high peak powers producing the dense plasmas. This technique is used for high-aspect-ratio trench filling applications. It also allows the improved target utilization and the get of a uniform thickness of the deposited films.

The development of the kinetic model of Ar/O2 will help to better understand the pulsed high power discharge. The model is based on the solving of mass balance equations of neutral and charged species coupled to the power balance equation. Therefore, it can track the densities of neutrals and ions considered in the reaction scheme as well as their flux in the substrate as function of time. In our model the power pulse has two types, the first one where the rise and fall times are represented by a linear relation, and the second one by an exponential law.

The simulations results show the effects of the main machine parameters, such as the pressure, the flow rates of O2 and Ar and the duty cycle, on the neutral and ion densities evolution versus time. On the other hand, the simulations show that, for the same average power, the dissociation and ionization rates in HiPIMS process are more efficient than those in RF PVD process.

Tilt and Strain distribution on GaP/Si by Scanning X-ray diffraction

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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 (semiconductor LED or laser[1,2,3] and integrated photonics devices[4]), as well as in the framework of the development of high-efficiency solar cells on low-cost silicon substrates or solar cell heterojunctions[5,6,7], and water splitting devices[8,9]. The GaP/Si provides a simple but important model system for the heteroepitaxial growth of polar semiconductor material on a nonpolar substrate, as the GaP is nearly lattice matched to Si. The structural quality of the GaP/Si pseudo-substrate has great influence on the photonic efficiency of the heterotpitaxial structure.

A synchrotron-based scanning X-ray diffraction study on a GaP/Si pseudo-substrate, within the context of the monolithic integration of photonics on silicon, will be introduced in the poster. Two-dimensional real space mappings of local lattice tilt and in-plane strain of the scattering spot distributions are measured on a 200 nm partially relaxed GaP layer epitaxially grown on a (001) Si substrate, using an advanced sub-micrometre X-ray diffraction microscopy technique (K-Map). 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, according to a comparison between in-plane strain mappings and transmission electron microscopy observations. The relationship between the in-plane strain and the free surface roughness is also discussed using a statistical method.

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Assessment of ciprofloxacin oxidation on hematite surfaces under flow-through conditions

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Ciprofloxacin (CIP) is one of the most widely used antibiotics which have emerged as contaminants of concern due to overuse[1]. Characterizing sorption and degradation processes is essential to assess the environmental distribution, persistence, and ecological significance of antibiotics in terrestrial and aquatic systems. Our previous study demonstrated that CIP, binds to nanosized hematite surfaces through inner-sphere bidentate complex and then redox reaction taking place over the reaction time generated several CIP by-products[2]. In this study, with the application of flow-interruption method and by-product track, non-equilibrium sorption and oxidation of CIP on hematite surfaces under flow-through conditions were investigated by column experiments. At low flow rate, CIP oxidation at hematite surfaces is highly expected and thus concomitant release of daughter products and ferrous iron from surfaces may enable free sorption sites and subsequently re-adsorption of CIP. Sorption and oxidation of CIP will be affected by the presence of it's by-products due to competition for sorption sites in the column system. In addition, modification in surface reactivity of hematite upon adsorption/oxidation of ferrous ion may take place. This work provided additional constraints to our growing understanding of the fate of antibiotics in the environment.

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