# Frequency comb generation in Interband Cascade Lasers

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Interband Cascade Lasers (ICLs) are semiconductor lasers emitting in the mid-wave infrared (MWIR 3-6 $\mu$m). They are practical laser sources for IR spectroscopy with milliwatts of output powers with low electrical power requirements, offering complimentary performances to quantum cascade lasers. Recent work has shown these ICLs can operate as frequency combs (FC)(1,2,3). Here we show a detailed study of FC ICLs coupled with adapted ultrafast Quantum Well Infrared Photodetectors (QWIPs), and correlating the microwave beatnotes with high resolution spectra of the ICL. In particular, we will show how the ICL transits from a FC to a dispersive regime that strongly effects the spectrum of the ICL.

In detail we realized a 2-section ICL operating at a wavelength of 3.8 $\mu$m, with its emission detected with a fast QWIP (response $>$ 20 GHz) operating at the same wavelength (Figure 1a & 1.b). Both structures operate at room temperature. The two section ICL constitutes a long section of 3 mm for laser action and a short section of 150$\mu$m to control the FC operation of the ICL. These are mounted on RF coplanar waveguides. Measuring a narrow beatnote (BN), electrically on the ICL or optically on the QWIP, is a preliminary measurement to determine if the ICL is operating in a FC regime. Figure 2 shows the electrical beatnote and its intensity as a function of ICL current. The corresponding spectrum shows that, as the beatnote widens with current, two sets of spectral lobes appear. We will show that this spectral lobes have different dispersive qualities, showing a complex interaction at mode proliferation in ICLs.

**Mots-Clés:** Interband Cascade Lasers (ICLs), frequency combs (FC), Quantum Well Infrared Photodetectors (QWIPs), mid, wave infrared (MWIR 3, 6 $\mu$m)

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*Intervenant

# Quo vadis, hydrogenium? Semiclassical and Quantum Algorithms for proton dynamics including Nuclear Quantum Effects

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Even if the laws of quantum mechanics are well known, the fundamental problem of quantum dynamics is the impossibility of resolution of the time-dependent Schrödinger equation for large systems, due to its exponential scaling with the number of degrees of freedom. One common step to deal with complex quantum multi-atomic systems is to assume an adiabatic separation between the electronic and nuclear time scales, considering the latter classically.
However, light nuclei show an intrinsic quantum delocalization which can be of the order of chemical bond lengths. Hence, Nuclear Quantum Effects can have a strong impact on chemical and physical properties. One notable example is the proton diffusion in solid materials. Light atoms 'tunnel' through barriers of potential energy surface, so to explore regions that would be classically forbidden, having significant impact on chemical reaction rates and transport. The first goal of my thesis is a critical comparison of different trajectory-based Molecular Dynamics methods as they provide computationally efficient approximations for treating light nuclei as quantum particle in complex environments. Only two limit cases can be exactly captured by most of approximated methods: the classical (high temperature) limit and systems with harmonic potential. Outside these scenarios, precise criteria for comparing different approximate methods are lacking. Ring-Polymer Molecular Dynamics, Quantum Thermal Bath and its refinement, the Adaptive QTB, are particularly relevant to this project.

The second objective of thesis is the application of these techniques to a real, condensed matter problem, namely the study of exotic phases of ammonia and water. These elements forms solid phases due to the extreme condition of pressure inside iced planets (Uranus and Neptune) cores. While individual ices of water and ammonia separately have been studied in great detail under pressure, the properties of their mixtures are much less explored.

**Mots-Clés:** Nuclear Quantum Effects, Molecular Dynamics, Proton Diffusion, Ammonia Hydrate ices

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*Intervenant

# Substrate Influence on the Stability of CsPbBr3 Perovskite Nanocrystals under UV-irradiation

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Electronic band structure and charge carrier dynamics of perovskites and their interface with different charge-transporting layers play a crucial role in defining the overall performance of optoelectronic devices (1,2). Inorganic Cesium lead bromide (CsPbBr3) perovskite nanocrystals (NCs) with a bandgap of 2.3 eV are considered one of the potential candidates as an active layer in solar cells devices and significant progress has been made in terms of improving its intrinsic properties and stability under environmental condition (3,4).However, stability under illumination with energy both below and above the bandgap remains mainly unexplored. Here, we have spin-coated CsPbBr3 NCs on two different substrates, gold (Au) and molybdenum oxide (MoOx) and investigate the influence of the substrate on the NCs stability under illumination using soft X-ray photoelectron spectroscopy. Depending on the substrate, NCs exhibit distinctly different behavior. When the NCs are exposed to laser pulses with the photon energy of 3.6 eV (greater than the bandgap), the NCs are irreversibly modified. Both metallic lead ($Pb^{o}$) and ionic lead (Pb+2) are seen in the Pb4f core-level spectra for both substrates as shown in Fig 1. The modification is more severe when NCs deposited on the Au substrate compared to on the MoOx substrate as evident by a stronger $Pb^{o}$ signal. Interestingly, on Au, not only does $Pb^{o}$ appear but a large chemical shift is also observed as the Pb4f is shifted by 0.59 eV towards higher binding energy. On the MoOx substrate, some $Pb^{o}$ is formed but no chemical shift is observed. Therefore, depending on the substrate, the CsPbBr3 NCs could have different energy level alignments. Consequently, it is of utmost importance to investigate interfacial energetics between CsPbBr3 NCs and different substrates under irradiation to better understand the underlying phenomenon that can aid in device design for improving device performance.

**Mots-Clés:** Perovskite, Nanocrystals, Stability, Radiations

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*Intervenant

# Design of heterostructured photoelectrodes for water-splitting

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Splitting water is one way to produce dihydrogen without side products that increase the global warming. However, a conventional electrolyser needs at least 1.23 V vs RHE to split the water molecule. Studies has been led to minimize the input of current by using photo-sensitive semi-conductors as electrodes. One of the challenges, in the development of performant tandem cell for water-splitting is the development of efficient, stable, photoanode, as the oxidation of water (OER, oxygen evolution reaction) reaction is the least favourable one. The photoanode material must fulfil several criteria to be efficient, starting with a band alignment allowing the OER reaction, absorption of light radiation in the UV-visible range and fast charge transport and finally a stability at near neutral pH (_~6). The objective of my thesis is to design, synthesize and characterise a bismuth vanadate-based photoanode that fulfil these criteria. Indeed, it is a semiconductor material, with a low bang-gap energy compared to other metal oxides (2.4 eV) with well positioned bands for OER. However, its two major drawbacks are 1) the low mobility of the photo-generated electron/hole charge carriers and 2) its instability at the pH used near the OER potential. Accordingly, my thesis work aims at designing a multilayer heterostructured electrode. To optimise the transport of photo-charges in the electrode, several strategies are studied: the control of the morphology of bismuth vanadate layer, its doping (Mo, W), the design of a heterojunction and an activation of the surface. Stability in acidic media is addressed by the use of a thin passivation layer. At the same time, the optimisation of solar radiation absorption should be possible by adding materials with refractive and light scattering properties (Bragg reflectors / plasmons).

**Mots-Clés:** water splitting, sustainable energy, photoelectrolysis

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# Persistent Luminescence Nanoparticles For Bioimaging in the NIR Window

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The persistent luminescence nanoparticles (PLNPs) emitting in the NIR-I (700–1100 nm) and NIR-II (1300–1700 nm) are able to avoid background noise. Several groups reported the use of PLNPs in preclinical studies(1). However, actually, no example of NIR-II is reported *in vivo*. The spinels (ZnGa2O4) and garnets (Y3Al2Ga3O12) doped with lanthanides (such as Ce3+, Nd3+ and Er3+) or transition metals (such as Ni2+ and Cr3+) (2-4) have been further optimized by the reduction of surface defects and ensuing longer afterglow in NIR range *via* glass-crystallization techniques and core-shell structure(5-7).
Recently, I prepared and transition metals (Ni, Sn) co-doped spinel (Zn1+xGa2-2x-ySnxNiyO4) PLNPs with a controllable emission wavelength in NIR range and modified their surface for effective passivation and better stability in aqueous solvent. The PLNPs could be well excited by UV and emit persistent luminescence at _˜1300 nm (Fig. 1B). The afterglow could be collected for more than 15 minutes in the NIR-II range. In addition, I developed 2 bio-windows imaging method based on the NPs co-doped with Cr3+. (see more details in the poster)
Towards the potential imaging application, the signal (from> 0.2 mg/ml of PLNPs in the water) could be obtained with the help of an InGaAs camera (Fig. 1C). In the near future, the PLNPs will be tested for *in vivo* imaging (Fig. 1D) by analyzing their extended emission in the tissue transparency, efficient functionalization, stability in aqueous and blood solution and persistent emission with different excitation sources.

**Mots-Clés:** Persistent Luminescence, Nanoparticles, Bioimaging, NIR Window

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*Intervenant

# Development of operando techniques for X-ray photoelectron spectroscopy study of the Solid Electrolyte Interphase formation in Lithium Ion Batteries

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In recent times, various technologies turned themselves towards batteries, and lithium ion batteries (LIBs) have then seen a rising importance in their role as a stable energy storage system. During the first charge and discharge cycles, a thin layer commonly referred to as the Solid Electrolyte Interface (SEI) is formed on the anode. While this leads to an initial capacity loss due to the consumption of Li+ in the reactions, this layer also prevents further degradation, allowing to exploit wider voltage ranges. Its stability it's also directly linked to the battery's life expectancy and safety. XPS is a very powerful technique for studying the SEI, giving precise information about the chemical composition, but its surface sensibility implies the need for the use of Ar+ sputtering to exfoliate the sample and expose the inner part to do depth profiling measurements, a method that bring changes to SEI composition. My project consists in the development of two techniques to approach XPS measures in-operando: on one hand, the development of a windowed cell for HAXPES measurements in SOLEIL based on some already existent electrocatalysis set-up will permit to measure the SEI from the electrode side without having to dismantle the cell and rinse the sample. On the other, using the dip&pull technique on an APPES (near Ambient Pressure PES) beamline will allow us to measure the SEI growth through the liquid phase. The two approaches will allow us to have a better understanding of what happens on the interphase between electrode and electrolyte while the SEI formation process happens, giving complementary information on the system. Both the two approaches had given initial results that will be presented on the poster along with more details on the choices made and the challenges faced.

**Mots-Clés:** sei lithium batteries electrochemistry xps

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*Intervenant

# Non-linear rheology of dynamic gels: spatial heterogeneities versus rheology

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Associative gels are temporary networks made of polymer chains connected by short-lived associations. They can yield and flow when submitted to external mechanical solicitations. These properties make them valuable materials in applications such as 3D printing, injectable gels for tissue reconstruction, or rheology additives for paints and coatings.

Whereas the linear properties of associative gels in the quiescent state or close to equilibrium have been widely studied both experimentally and theoretically, much less is known about their behavior under large deformation. Several fascinating phenomena have been reported - fracture, shear banding, wall slip, self-healing, chaotic motion – but the relation between these deformation mechanisms and the strength of the inter-chains associations is still missing. Here we take on this challenge using a family of associative polymers comprising a polyelectrolyte backbone and lateral pending blocks made of a hydrophilic spacer and a hydrophobic alkyl group. The hydrophobic groups form micelles that connect the polymer chains. The strength of the associations is tuned at will by changing the length of the alkyl groups.

When the alkyl groups comprise 16 carbon atoms or less, the polymers solutions are viscoelastic liquids that flow homogeneously. When the number of carbon atoms increases new properties appear. For 32 carbon atoms, gelation occurs at a well-defined polymer concentration. The non-linear rheology of gels depends on the experimental protocol and the history of applied deformation. To understand this rich and complex behavior, we have performed a multiscale rheo-optical analysis combining macroscopic rheology and in-situ measurements of deformation profiles using a home-made fluorescence microscope. We are able to observe and disentangle multiple flow mechanisms such as wall slip and transient shear banding. These results open the route to a systematic understanding of the flow properties of these associative gels in relation with the strength of the associations.

**Mots-Clés:** gels, physical gels, hydrogels, associative groups, hydrophobic interactions, temporary crosslinks, physical crosslinks, rheology, linear rheology, non linear rheology, particle image velocimetry, velocity profile, flow curve, frequency sweep

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# Development of a hybrid electrolyte for lithium metal solid-state batteries

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Increasing demand for electrochemical energy storage goes hand in hand with the ongoing energy transition. If the Lithium-ion battery is currently the prevailing technology, shifting from a flammable organic liquid electrolyte to a solid-state lithium ionic conductor would allow safer and lighter batteries, with the use of Li-metal at the anode. Yet, solid-state batteries are still facing challenges to compete with Li-ion ones. One of them is the chemical and mechanical instability of the interface between the ductile Li-metal and the compressed-powder solid electrolyte layer. Shifting from a pure inorganic separator to a hybrid electrolyte is our strategy to overcome this issue, taking the best of polymer electrolytes (processability, mechanical integrity, stable interface with Li-metal but low conductivity) and inorganic electrolytes (high room-temperature conductivity but brittleness). Using argyrodite-type Li6PS5Cl particles embedded in a PEO:LiTFSI polymer electrolyte matrix, the composite is formulated *via* a dry process to reach a compromise between Li+ conductivity and mechanical integrity, without solvent contamination. In the present study, we discuss the influence of the organic-to-inorganic ratio and the PEO molecular weight on the activation mechanism of the composite ionic conductivity and its mechanical properties. A crucial characteristic to achieve, along a sufficient conductivity (> 10^-4 S.cm-1), is the effective thinning of the membrane (< 100 $\mu$m) by calendering, to ensure a scalable process. To understand the composite chemical stability, X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (ssNMR) are performed to identify interfacial products between the organic and the inorganic phases. The resulting interfacial resistance is quantified according to temperature. Alongside the formulation and reactivity study, the processing and assembly aspects are investigated with a focus on the Li metal | composite electrolyte interface and its optimization for better cycling performances.

**Mots-Clés:** hybrid solid electrolyte, argyrodite, polymer electrolyte, lithium metal, interfaces stability, all solid state batteries, electrochemical impedance spectroscopy

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*Intervenant

# Cross-linked polyethylene copolymers by reactive extrusion using vitrimer chemistry

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Industrial thermoplastics like polyethylene (PE) can be cross-linked through vitrimers chemistry1 to obtain materials with improved thermal and mechanical properties while keeping reprocessability.2 Starting from PE-glycidyl methacrylate copolymers, we present some strategies of transformation into polyolefin-based vitrimers using catalysed epoxy-acid addition and/or transesterification.Chemical and physical evolution of the networks during sol-gel transition are investigated using infrared spectroscopy coupled with simultaneous multifrequency strain rheology3, allowing to accurately detect the gel point and the degree of conversion for different degree of functionalization.

The final materials exhibit improved thermal and solvent resistance, due to both crystalline domains and cross-links. When being submitted to high pressure digestion in a reactive solvent mixture, the network can be decrosslinked, demonstrating the reversibility of the crosslinks. Bulk network dynamics are also evaluated in relation to their chemical structure to investigate how dynamic bonds can rearrange when an external stimulus is applied.

**Mots-Clés:** Vitrimers, Polyolefins, Reactive Extrusion, Transesterification

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# Understanding the flow of a foam in a porous medium

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Injecting foam in a porous medium is a method widely used for many applications, for example soil remediation, CO2 capture and storage or enhanced oil recovery. But the foam behavior and the parameters impacting its properties are far from being fully understood. In particular, the influence of the surfactant used is big but cannot be predicted by bulk experiments. The goal of my thesis is to develop simple surfactant screening tests but also to improve the understanding of the physical mechanisms involved. For this, I developed simple and model experiments in micro- and milli-fluidic to study the key aspects of the flow of foam in a porous medium.

**Mots-Clés:** foam, porous medium, microfluidic

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*Intervenant

# Photonic antennas to boost the light and chiral matter interactions

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Sensitivity to molecular chirality is crucial for biology and chemistry to the pharmaceutical industry. Unfortunately, current enantiomeric selection techniques rely on expensive, slow, high-volume systems and are effective mainly in the UV. Nanophotonics brings innovative solutions to these problems via the generation of superchiral light in the near field, characterized by the chirality density (C), allowing for a reduction of the detection volume and a higher sensitivity. In most cases, the distribution of C around the photonic nanostructure is not uniform, diminishing the interest of the nanophotonic approach.

I have simulated the electromagnetic nearfield properties of various plasmonic nanostructures using FDTD (Lumerical). I have shown that nano-apertures excited with linear polarization were efficient nanostructures allowing the control of the sign of C with an unprecedented uniform distribution of C. In agreement with the Babinet's principle, I have shown that the main properties of nano-apertures can be captured by using a magnetic point-like dipole model. In particular, the polarization angle and the spectral dependence are very well reproduced and explained. Therefore, plasmonic nano-aperture allow transforming a linearly polarized farfield light into a localized chiral light that will couple to the chiral molecules. This type of resonators could be used as sensing elements for the ultrasensitive detection of chiral molecules.

To go further in the study of the electromagnetic interaction of chiral molecules with nano-apertures, I am currently developing an original measurement setup combining modulation of polarization and mirco-fluorescence. The aim is to characterize the CD of fluorescent test chiral molecules placed in nano-apertures by monitoring the intensity of their fluorescence. The combination of excitation from the farfield with linearly polarized light together with monitoring the emission should yield very sensitive measurements of CD, at leats at the level of the single nano-aperture.

**Mots-Clés:** Magnetic dipole nano, antenna, superchiral light, plasmonics, nanophotonics, achiral nanostructures, fluorescence

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*Intervenant

# Collagen/hyaluronan dense hydrogels developed by 3D bioprinting to model the intervertebral disc and its degeneration

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50% of back pains are due to intervertebral disc (IVD) degeneration. Treatments are not effective for the disc regeneration because they are only short-term solutions to relieve pain. The reason why there is no efficient treatment for this pathology is the lack of knowledge and understanding. Hence, there is a need to develop novel 3D in vitro models to unravel the pathophysiology of disc degeneration. As IVD is mainly composed of collagen and glycosaminoglycans, a novel model made of type I collagen and hyaluronic acid would be of great interest.
In that scope, our goal was to develop a novel IVD 3D in vitro model composed of type I collagen and tyramine functionalized hyaluronic acid (THA) obtained by 3D bioprinting.

Our main challenge was to obtain homogeneous collagen/THA hydrogels with optimal physical properties. When THA and collagen are mixed together, they instantly interact to form polyionic complexes (PIC), visible as aggregates. After studying their physico-chemical behavior, we managed to formulate a homogeneous collagen/ hyaluronic acid bioink by adding salts and modulating the pH of solution, leading to the formation of enhanced hydrogels in terms of thermal structural and mechanical properties after double gelation.

The second part of this PhD focused on 3D bioprinting. The previously developed formulation was used for 3D printing. All the printing parameters (speed, temperature, gelling conditions and extrusion pressure among others) were optimized in order to get a homogeneous enhanced scaffold compatible with the tissue engineering application targeted. Finally, cells will be seeded on this scaffold either over a single printed layer either in a sandwich conformation between two layers in order to assess the viability of our novel IVD in vitro model.

**Mots-Clés:** collagen, hyaluronan, polyionic complexes, 3D printing, intervertebral disc

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Abstract

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*Intervenant

# A single 2D particle for bi-color down-conversion.

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Nanocrystals (NCs) are now established building blocks for optoelectronics and their use as down converters for large gamut displays has been their first mass market. NC integration relies on a combination of green and red NCs into a blend, which rises post-growth formulation issues. A careful engineering of the NCs may enable dual emissions from a single NC population which violates Kasha's rule, which stipulates that emission should occur at the band edge. Thus, in addition to an attentive control of band alignment to obtain green and red signals, non-radiative decay paths also have to be carefully slowed down to enable emission away from the ground state. Here, we demonstrate that core/crown/crown 2D nanoplatelets (NPLs), made of CdSe/CdTe/CdSe, can combine a large volume and a type-II band alignment enabling simultaneously red and narrow green emissions. Moreover, we demonstrate that the ratio of the two emissions can be tuned by the incident power, which results in a saturation of the red emission due to non-radiative Auger recombination that affects this emission much stronger than the green one. Finally, we also show that dual-color, power tunable, emission can be obtained through an electrical excitation.

**Mots-Clés:** 2D semiconductor nanocrystals, Colloidal synthesis, Bicolor emission, Power tunability

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*Intervenant

# Synthesis and Characterization of Nanorods and Thin Films of ZnO for Photocatalytic Applications

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As global industrialization continues to grow (7.2% in 2021), discharged wastewater became a major concern jeopardizing nowadays ecosystem. Particularly, loaded effluents with persistent toxic molecules from refineries, petrochemical, pharmaceutical, plasticizer, and many other industries, are continuously endangering surface and groundwater water sustainability. With the low efficiency of conventional treatment techniques in addressing the removal of a wide spectrum of these toxic chemicals, advanced oxidation processes (AOPs) have emerged as an efficient, promising, and inexpensive technology, capable of tackling different types of organic molecules in aquatic mediums. Among these AOPs, photocatalysis is considered one of the most practical methods that have proven its efficiency due to its low cost, reusability, and no requirement for secondary disposal methods. An ideal photocatalytic material provides simultaneously, a strong oxidation ability and low production cost. For that reason, this ambitious thesis program aims first to design nanostructured films of zinc oxide (ZnO) with controlled morphology and porosity via different routes such as sol-gel dip-coating, spray, and hydrothermal growth to study the effect of the material structure on its photocatalytic activity. This latter was tested on Methylene Blue probe molecule and on recalcitrant molecules such as Phenol. To extend the efficiency boundaries of the ZnO photocatalyst, the latter was coupled with a cost-effective photo Fenton-like process. A lab-scale prototype is meant to be designed based on the collected kinetic data.

**Mots-Clés:** Photocatalysis, Zinc Oxide, Thin Films, Sol, Gel Dip, Coating, Hydrothermal Growth, Photodegradation kinetics, photo, Fenton

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# MOLTEN SALT SYNTHESIS OF NICKEL BORIDE NANOPARTICLES: MECHANISMS AND ELECTROCATALYTIC PROPERTIES

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Transition metal borides are of high interest for the production of dihydrogen by electrocatalysis of water splitting, due to their catalytic activity and their resistance to corrosion.(1,2) These materials are generally obtained by high temperature solid state reaction (> 1000∘C) between the constituent elements.(1,4) These processes are not adapted to the elaboration of nano-objects, which present higher activity in catalysis.(3,4) At lower temperatures, the syntheses in solvents only leads to amorphous nanoparticles.(1,5) Some approaches in liquid media at high temperatures have been proposed, but suffer from a very limited control of the nano-object size and crystal structure. (1,6,7) The elaboration of crystalline nanomaterials would allow a better understanding of the structure-properties of catalysis, but also improve the stability of the catalysts.

We will present a new synthesis approach, consisting in activating the reactivity of metals towards boron incorporation. This is achieved by combining two approaches. First, we use metallic nanoparticles as nanoreactors. Second, we carry the reaction in molten salts; stable liquids at high temperature (475 ∘C). We will show how to control the incorporation of boron in nickel nanoparticles to selectively form the first Ni3B and Ni4B3 nanocrystals. By combining *ex situ* techniques (X-ray scattering based methods, transmission electron microscopy) and *in situ* X-ray diffraction in molten salts, we will discuss the nature of the intermediate states of these reactions and their evolution.

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# Understanding Morphological Transition in Polymerization-Induced Self-Assembly: is Unimer Exchange necessary?

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The Polymerization Induced Self-Assembly (PISA)(1) occurs in aqueous medium when a hydrophobic polymer block (block B) is synthesized from a hydrophilic one (block A). As the B block grows, the formed amphiphilic polymer chains self-assemble into nano-objects whose shape is defined by thermodynamics. It has already been reported that the self-assemblies evolve from spheres to fibers and eventually vesicles when the size of the B block increases during the polymerization(2). Such morphological transitions can occur through fusion(3) of nano-objects or through unimer exchanges(4), which imply the displacement of single polymer chains through the aqueous medium from one hydrophobic core to another. Assessing the role of the exchange dynamics and trying to tune it is the core this thesis.
Combining a systematic study of a representative PISA system with rheological measurements, we demonstrate here that unimer exchanges are not necessary to evolve towards higher order morphologies. Instead, we proved that the free monomer present in the synthesis medium allows the morphological transitions through fusions, even though it slows down the exchange dynamics at the same time.

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# Direct Imaging of Micrometer Thick Interfaces in Salt-Salt Aqueous Biphasic Systems

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Unlike the interface between two immiscible electrolyte solutions (ITIES), such as water with polar solvents, our molecular understanding of the liquid/liquid interface formed for aqueous biphasic systems (ABS) is relatively limited and mostly relies on surface tension measurements and thermodynamics models. Here Raman imagining is used to provide spatial and chemical resolution at the interface of LiCl-LiTFSI-water and HCl-LiTFSI-water salt-salt ABS. The concentration profiles for both TFSI anions and water are found to be a sigmoid curve, in agreement with the increasing surface tension as function of concentration, both being typical of a negative adsorption mechanism. More striking is the length at which the concentration profiles extend, ranging from 11 to 2 mm with increasing concentrations, compared to tens to hundreds of nm for polymer ABS. We thus reveal that unlike ITIES, salt-salt ABS do not have a molecularly sharp interface but rather form an interphase with a gradual change of environment from one phase to the other. This knowledge represents a major step stone in the understanding of aqueous interfaces toward dynamics and mastering of ions or electrons transfers across ABS's interface.

**Mots-Clés:** Raman, Micrometer interfaces, Aqueous Biphasic Systems

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# Understanding the destabilization of oil foams

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Industrial processes involving liquids often face unwanted foaming issues which are solved by adding anti-foaming agents. On the other hand, the development of electric car engines has challenged the formulation of new lubricants. Indeed, these engines operate at high rotation speed, which favors the production of foam in gears and, as a consequence, a drastic decrease of the lubricant efficiency. Classical antifoaming additives are thus used but, surprisingly, they sometimes lead to a pro-foaming effect in new lubricant formulations. Moreover, whereas the destabilization of aqueous foams using these additives has been extensively studied (1), the mechanisms at stake in the case of oil foams is still poorly understood.
Our goal is to develop a comprehensive description of the antifoaming effects of immiscible liquid droplets added to oils (2) in order to account for the effect of different properties such as surface tension, viscosity or solubility on the dynamics of foaming and anti-foaming.

Using a ternary mixture of oils including Polydimethylsiloxane (PDMS), we first obtain an emulsion of PDMS-rich microdroplets resulting from a spontaneous emulsification. We show that the microdroplets coalesce in the bulk without delay due to Brownian motion. Then, we use surface tension measurements to probe the behavior of the emulsion at an air interface. We show that the droplets enter the oil/air interface without delay and spread at this interface creating a thin layer of PDMS (3). Finally, using a thin film balance experiment, we study the consequences of this observation on the stability of a thin emulsion film.

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**Mots-Clés:** emulsion, air, coalescence, surface tension, thin film

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# Sodium-ion batteries: Hype, Hope or Reality?

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Lithium-ion batteries (*LIBs*), first commercially developed for portable electronics, are now ubiquitous in daily life, with increasingly diverse applications, including electric vehicles (*EVs*), smart grids, medical devices, satellites, etc. In 2020, for the first time, the global number of EVs on the road surpassed 10 million, with 3.2 million *EVs* sold in 2020 alone, reflecting enormous demand for LIBs. Though exciting transition, the limited lithium sources and their uneven distribution necessitate the development of complementary, low-cost, and sustainable battery technologies. Sodium-ion batteries (*SIBs*) that share similar chemistry and the same production and engineering units with LIBs are expected to fill this gap. However, a slight change of shuttling ion from Li+ to Na+ significantly affects the working chemistry and energetics of the cell. Moreover, having the optimum electrode materials, the commercial success of the battery chemistry is solely governed by the electrolyte. The thesis is focused on systematically studying the challenges in designing the suitable electrode-electrolyte interfaces(*EEI*) of the Na3V2(PO4)2F3 (*NVPF*) and hard carbon (*HC*) as positive and negative electrodes, respectively. The *NVPF* positive electrode has enormous issues of electrolyte oxidation because of its high operating potential (_˜4.20 V vs. Na+/Na0 or equivalent to 4.53 V vs. Li+/Li0). Concomitant to electrolyte oxidation is the challenge of vanadium dissolution in the electrolyte, which deteriorates the *NVPF* material and poisons the *EEIs.* On the other hand, the solid electrolyte interface(*SEI*) formed on *HC* is highly soluble on account of soluble Na-based compounds. After a fundamental understanding of the cell degradation, the optimum electrolyte is developed, which showed superior cell performance in commercial type NVPF-HC cylindrical 18650 cells. Finally, the presentation will conclude with the commercial prospects of different *SIB* chemistries and their comparison to the already commercialized giant *LIBs.*

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# Triazines: a novel chemistry for the synthesis of dynamic network

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The need for light but tough materials has induced an increase in plastic demand. To obtain outstanding mechanical properties and solvent resistance, thermosets are needed. However, their covalently cross-linked nature results in a loss of processability and recyclability. To bypass these issues, vitrimers were introduced. They are covalent adaptable networks (CANs) with a temperature independent cross-linking density. Upon heating, degenerate exchange reactions allow the network to change its topology to release stress. The material can then be processed at high temperature but keep their shape at low temperature.
A variety of dynamic cross-links have already been developed to design vitrimers. In this work, we study a new exchange chemistry to access such CANs. It relies on the degenerate exchange between phenoxide ions and phenoxytriazines. The exchange was first studied by NMR in solution on model molecules. An activation energy of 86.9 kJ/mol was obtained in toluene for example. Thanks to the modularity of the triazine core, different substituted phenoxytriazines were synthesized and are being studied.

This novel chemistry was also implemented in materials. A poly(styrene-co-hydroxystyrene) copolymer was synthesized. Upon solubilization of the copolymer in a solvent, addition of a base and triphenoxytriazine, a gel was formed at room temperature. After drying, the obtained material could be extruded and processed. It was later studied by rheology. Dynamic mechanical analysis (DMA) showed the presence of a rubbery plateau similarly to a thermoset. The importance of non-covalent ionic aggregation and physical cross-linking resulting from ionic interactions were highlighted, even at low ionic content.
This work expands the library of dynamic exchange chemistry for CANs. The low cost of products and molecule tuning possibilities could help push for the introduction of vitrimers in real life applications.

**Mots-Clés:** vitrimer, triazine, phenol

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# Combining Machine Learning Approaches and Accurate Ab Initio Enhanced Sampling Methods for Prebiotic Chemical Reactions in Solution

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The study of the thermodynamics, kinetics, and microscopic mechanisms of chemical reactions in solution requires the use of advanced free-energy methods for predictions to be quantitative. This task is however a formidable one for atomistic simulation methods, as the cost of quantum-based *ab initio* approaches, to obtain statistically meaningful samplings of the relevant chemical spaces and networks, becomes exceedingly heavy. In this work, we critically assess the optimal structure and minimal size of an *ab initio* training set able to lead to accurate free-energy profiles sampled with neural network potentials. The results allow one to propose an *ab initio* protocol where the *ad hoc* inclusion of a machine-learning (ML)-based task can significantly increase the computational efficiency, while keeping the *ab initio* accuracy and, at the same time, avoiding some of the notorious extrapolation risks in typical atomistic ML approaches. We focus on two representative, and computationally challenging, reaction steps of the classic Strecker-cyanohydrin mechanism for glycine synthesis in water solution, where the main precursors are formaldehyde and hydrogen cyanide. We demonstrate that indistinguishable *ab initio* quality results are obtained, thanks to the ML subprotocol, at about 1 order of magnitude less of computational load.

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# Study of graphene/ionic liquid interfaces using the Langmuir procedure

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Supercapacitors devices based on graphene as electrode and ionic liquid as electrolyte are promising devices for energy storage. Their operating concept is based on the principle of storing electrostatic charges at the level of the electrode/electrolyte interface. Supercapacitors exhibit high capacitance so can accept and deliver charges much faster than capacitors and batteries. The performance of supercapacitors is limited due to the restricted access of electrolyte ions to the electrode. To understand the access mechanism of ions to the electrode its necessary to form electrode/electrolyte interface. Langmuir procedure is used for controlling the formation of two-dimensional films. It's therefore adapted to form such interface. So, mixture of graphene oxide (GO) and ionic liquid (IL) solution are spreading on water surface by Langmuir procedure. Thanks to this method it's easy to access to the interface between GO and IL and follow the evolution of the film by several technique: Isotherm, Brewster angle microscopy (BAM), Grazing incidence X-ray diffraction (GIXRD), X-ray reflectivity (XRR), X-ray fluorescence (XRF) and atomic force microscope (AFM). Then get information about how the nature of the environment surrounding the ionic liquid film modify the interaction and can improve the energy density of supercapacitors.

**Mots-Clés:** Graphene Oxide, Ionic Liquid, Langmuir film, supercapacitors

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# Mechanical and electronic properties of metallic nanoparticle

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At the nanoscale, physical properties change with size. For example, it is well known that electronic properties change from those of bulk materials to those of potential wells. This effect has also been observed in mechanical properties. ”Smaller is stronger” is the motto expressing the increased strength associated with smaller nanostructures. In this project, we are interested in the interplay of shape, size, electronic and mechanical properties of nanomaterials. To study the mechanical properties of metal and alloy nanoparticles (NPs), we use a multiscale and multiphysics approach combining atomistic (Molecular Dynamics) and continuous methods (Finite Element). The method was developed on model materials (Au, Cu, and Pt), and the analysis has now shifted to more complex structures (ordered and disordered CoPt nanoparticles). The underlying reason for studying nanoindentation using MD and FE is the computation time, which severely limits the applicability of MD for modeling large NPs. The study highlights two key findings. First, we have demonstrated the effectiveness of the nanoscale FE solution due to comparisons with MD simulations. Furthermore, a strong dependence of the elastic properties on the shape of the nanoparticles was found. Recently, the same methods (FE and MD) have been used to characterize the mechanical properties of bimetallic CoPt NPs, comparing ordered structures with mixed crystals. In the second part, the electronic properties of deformed NPs are investigated using a tight-binding model based on the Green’s functional form. Using pure Pt nanoparticles as an example, we show how the electronic properties change upon deformation. Special attention was paid to analyzing the local density of states of surface atoms. Therefore, we will show how some specific surface sites become particularly sensitive to catalytic reactions after plastic deformation.

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# Drying of a thin film of complex fluid under an evaporation mask

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Wet coating consists in spreading a liquid film containing particles or polymers on a substrate and letting the solvent evaporate. It is of great interest for industry as it is cost effective and allows the functionalization of substrates with a broad range of materials. However, whilst drying, evaporation flux heterogeneities spontaneously appear at the edges. This can deform the surface and generate flows in the film, leading to a non-flat deposit in the end.

These evaporation flux heterogeneities being difficult to quantify, we use an evaporation mask located just above the film to impose a controlled heterogeneity of the evaporation flux. Experimental studies have shown that a marked depression appears in the dried film below the mask location (1,2). Qualitatively, the solvent evaporates faster in the unmasked area, which deforms the surface and generates flows. These outward flows carry solute away from the mask, which explains the observed depression. This mechanism has been exploited in the last decade in order to obtain deposits of given shapes but is not quantitatively described in the literature (3).

We study both experimentally and theoretically the effect of an evaporation mask placed above a drying film of polymer / solvent solutions. We find analytical solutions for the final shape of the polymer layer considering that either gravity or capillarity drives the flows. We demonstrate that gravity can play a role in these deformations even for films with an initial thickness that is smaller than the capillary length. Our predictions are in good agreement with experimental results obtained with solutions of polystyrene in toluene. A typical experimental profile of the dried film is shown on Figure 1(a). The analysis we have conducted therefore offers the first quantitative prediction of the shaping of a deposit with an evaporation mask.

**Mots-Clés:** wet coating, evaporation, polymers

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# Structural characterization by Solid-State NMR of carbonate & silicate substituted hydroxyapatites

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Bone deficiencies can arise from various causes (age, diseases, accidents, etc.). The idea of making synthetic bone implants that can be grafted so that the patient's body degrades them and uses the products to recreate bone has been under study for many years.

The mineral part of human bone is structurally very similar to hydroxyapatite (HA). In biological environments, the differences with HA arise from the anionic and cationic substitutions that occur in response to the various functions of bone tissue. The incorporation of carbonate ions (CO32-) into the HA structure modulates the resorption and dissolution properties, which are key factors in the success of bone repair. On the other hand, silicate (SiO44-) substitution would have positive effects on biocompatibility and bone calcification. Thus, hypothetically, the simultaneous incorporation of carbonate and silicate ions into the apatite structure (CSiHA) would allow coupling the resorption and dissolution properties of carbonates with the important metabolic role of silicon in connective tissue.

Samples were synthesised according to strict protocols. They were obtained by co-precipitation of different precursors (Ca(NO3)2, 4H2O; (NH4)2HPO4; Si(OCH2CH3)4 enriched in 29Si) to lead to an isotopically enriched silicate substituted hydroxyapatite. Then, different thermal treatments such as annealing at 1000◦C or gaseous carbonatation (750◦C under 13CO2) were applied to obtain silicate or carbonate & silicate substituted HA.

Thanks to the isotopic enrichments performed during the synthesis, two-dimensional multinuclear experiments can be performed to localize the carbonates and silicates within the apatite lattice, and to propose structural models for these substituted HA as well as substitution mechanisms. In addition, the biological responses of the various samples studied could be related to the position of these substituents on an atomic scale.

**Mots-Clés:** Hydroxyapatite, Solid, State NMR, Structural characterization, Biomaterial

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# Ecologically efficient synthesis of heterogenous catalysts via solvent-free reactive extrusion

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We present a new strategy for the synthesis of sustainable manufacturing catalysts, which combines the sol-gel process with the principle of reactive extrusion. This method allows simultaneously the formation and shaping of the active phase and the support, at room temperature in a solvent-free continuous mode. Reactive extrusion has been intensively developed for the synthesis and processing of polymeric materials but it is still in its beginning stage for metal oxides. We focused on the synthesis of bohemite ($\gamma$-AlOOH) which is converted upon calcination into mesoporous alumina ($\gamma$-Al2O3) with high specific surface area. This oxide is widely used in industry as catalyst and catalyst support. As-obtained material exhibits good catalytic properties regarding ethanol dehydration activity comparable to those observed in literature. Afterwards, we developed reactors and processes for the synthesis of Ruthenium-based catalysts supported on $\gamma$-AlOOH and $\gamma$-Al2O3 for CO2 methanation. In order to quickly evaluate the influence of the experimental parameters (concentrations, temperature and hydrolysis), the simultaneous synthesis of the support and the active phase of the catalyst was developed in a stirred reactor tank (outside the extruder). The Ru precursor is mixed with the Al precursor without addition of solvent then the mixture was hydrolyzed with a stochiometric quantity of water. Ru/AlOOH catalysts with Ru weight contents wt%Ru 2 and 6% were prepared. The obtained materials exhibit dispersed Ru clusters and NPs of 3-5 nm on $\gamma$-AlOOH with promising CO2 methanation activity: 100% CH4 selectivity with a production rate of 33 mmol.g-1.h-1 and a conversion upper to 66% at 300 $\circ$C catalysis temperature (for wt%Ru 6% reduced at 200 $\circ$C).

**Mots-Clés:** Sol gel, Solvent free, Green synthesis, Reactive extrusion, Alumina, Bohemite, Ruthenium, CO2 methanation, Catalysts

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# ULTRAFAST TERAHERTZ PHOTOCURRENTS IN SEMI-METAL AND SEMICONDUCTOR FEW LAYER PTSE2

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A breadth of 2D transition metal dichalcogenides (TMD) semiconductors has been investigated in recent years, each with unique bandstructures that are distinctly different from the bulk. Some of the most commonly studied materials include MoS2, WS2, MoSe2, and WSe2, and key features include tunable bandgap energies in the optical region. On the other hand, the recently discovered TMD PtSe2 has garnered considerable interest owing to its relatively high electron mobilities Further the layered controlled bandgap can tune from an indirect semiconductor to a semi-metal, covering a vast energy scale, from the near-infrared for monolayers to the terahertz (THz) region for multiple layers.

The project investigates THz intra- and inter- layer carrier dynamics and transport mechanisms in PtSe2, where a femtosecond optical excitation permits to generate photocurrents that are probed using terahertz time domain spectroscopy (THz-TDS). Here, the PtSe2 is excited with a 100fs, 800nm Ti:Sapphire laser for the ultrafast generation of interband carriers, generating a time varying current that radiates as a THz single cycle pulse.We demonstrate the THz emission from this material for the first time and show that this is a result of second order nonlinear photocurrents in PtSe2, with contributions from photon drag and photogalvanic effects. We will show how the PtSe2 bandstructure dependence on the number of 2D layers radically changes its THz emission properties, rendering PtSe2 a promising material for THz photonics. Thanks to bandgap engineering of PtSe2, the potential use of this material integrated with MIR lasers will be also studied.

**Mots-Clés:** PtSe2, Time domaine spectroscopy, Terahertz, TMD, 2D material

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*Intervenant

# Interfacial engineering to solve interface issues within all-solid-state batteries

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The need to store energy is not new. Indeed, for more than 100 years already, dams and pumped-storage hydroelectricity facilities have been used to store excess electricity and balance the load on the electrical grid. However, in a world shifting towards renewable but intermittent energy sources and electrified vehicles, energy storage devices are becoming increasingly important.
Electrochemical energy storage devices, such as the rechargeable Lithium-ion battery (LIB) technology, are currently one of the best solutions to this energy storage challenge. Widely used in mobile devices and more recently in electric vehicles, state-of-the-art Li-ion batteries offer, until now, sufficient performances for most of their usage. However, there is an ever-increasing demand for batteries with even higher energy density, power and efficiency to improve or even unlock new applications, most notably for transportation and grid-scale stationary storage.

All-solid-state batteries (ASSBs) are currently regarded as a possible alternative to conventional LIBs with liquid electrolyte, due to their expected higher energy densities and higher safety. Unfortunately, the implementation of ASSBs in real systems is plagued by great challenges. Among them are the interfacial issues at both electrodes that are nowadays heavily studied within the ASSB field and that are exacerbated with lower cycling pressures.
Hence, great efforts were first devoted at reducing the amount of interfaces at both electrodes, with the implementation of lithium metal or silicon at the negative and of the highly ionic and electronic sulfide-based phases at the positive electrode such as O3-LixTiS2 (LTS). While in a second time, optimisation of the cathode composite was successfully performed and allowed a significant decrease of the cycling pressure from 100 to 0.1 MPa.

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*Intervenant

# TERNARY NANOCRYSTALS AS ELECTROCATALYSTS FOR WATER SPLITTING

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Among non-oxide compounds of transition metals and p-block elements, transition metal (TM) borides have been some of the last solids emerging in the last years as efficient catalysts or pre-catalysts for electrochemical water splitting (H2 evolution and water oxidation reactions) and CO2 reduction (1,2). Transition metal silicides have also appeared very recently as pre-catalysts for water oxidation (3,4). In borides and silicides, the strong bonds between TM and B or Si influence the charge density around the metal atom and the local geometry, which deeply impact catalytic properties. The combination of not only one but two metalloids with TMs could further boost catalytic properties, especially when size, morphology and the geometry of surface sites can be tuned. However, transition metal silicoborides are rare (5), their properties are unknown, and they require large input of energy to trigger crystallization. These conditions strongly favour crystal growth over nucleation, which makes the preparation of nanostructures particularly hard, although they would be ideal candidates to develop high surface-to-volume catalysts.

In this work, we report the first synthesis of TM silicoborides nanocrystals and a general synthesis approach towards this rare class of materials. By using eutectic salt melts as liquid reaction media, the nucleation of nanoparticles is promoted and their growth limited. *In situ* XRD measurements carried out at synchrotron beamlines reveal the crystallization sequence from metal salts to metals, binary and then ternary phases. We measured promising electrocatalytic properties and show how the metalloids influence the charge density of the metal atom by XPS.

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**Mots-Clés:** Nanocrystals, silicide, boride, ternary, electrochemical water splitting

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# ZnO ultra-thin films as a case study for polarity and doping interplay at the nanoscale

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Zinc oxide is a large direct band-gap semiconductor widely used in numerous of fields such as cosmetic, optoelectronic, or catalysis. It's usually doped with group III atoms like Al, Ga, and In, which increased n-type conductivity. Aluminum doping is notably used to produce a conductive and transparent thin film that could be used to develop low-emissivity glass or flexible display panels. To maximize the conductivity, without reducing transmission in the visible wavelength, the optimum doping rate is around 2-3%. The general view it's that dopant is primarily localized in zinc substitutional sites and beyond a certain doping rate, it could start to occupy interstitial sites. However, the optimum conductivity doping rate is highly dependent on the synthesis method and post-synthesis treatment. It was notably reported that new phases could appear and hinder charge transport. The first aim of this work is to investigate the influence of several parameters – like substrate synthesis (ZnO or Si), target material (metallic or ceramic), and atmosphere during thermal treatment – on the chemical environment of Al. We have studied AZO thin film, synthesize by sputtering deposition, with several characterization techniques such as photoemission and absorption X-ray spectroscopy (XPS and XAS), X-ray diffraction (XRD), and atomic force microscopy (AFM). It has already been revealed surface segregation of Al after high-temperature annealing. Furthermore, the chemical environment of Al seems to be affected only by annealing under an oxidant atmosphere and Si-supported film. Zinc oxide is also a polar oxide, known to present healing polarity mechanisms to stabilize their polar faces. We also explore the influence thickness of ZnO and Mg doping on these phenomena. For this part, we synthesized ZnO layers in Ag and Pt monocrystals, that we characterized in situ by XPS, low energy electron diffraction (LEED), and scanning tunneling microscopy (STM).

**Mots-Clés:** Al doped ZnO, Photoemission, Surface Sciences, Photoemission, Scanning Electronic Microscopy.

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# Mid Infrared Photodetection with Nanocrystals

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The infrared is a part of the electromagnetic spectrum with wavelengths longer than the visible light. This domain brings complementary information to the visible one. The infrared finds its application in astronomy, defense and civilian field with LIDAR (autonomous vehicle), face recognition and even industrial vision. While the silicon-based photodetection technology rules over the visible market, their equivalent has yet to be developed in the infrared. For long, the latter was dominated by epitaxially grown III-V and II-VI semiconductors, but their fabrication led to a high cost. However during the past decade, nanocrystals, a new emerging technology, have shown that they could combine high-performance and low cost to address the infrared range (1). In particular in the short infrared (1-2.5 $\mu$m) by using narrow band gap colloidal semiconductors such as HgTe (2-3). In this work, we will go beyond and access the mid infrared (3-5 $\mu$m) with the design of a nanocrystal-based heterostructure. Throughout an original approach where we couple an intraband absorber (HgSe) to an undoped material (HgTe) driving the charge conduction, we rule out the limitations typically observed in intraband materials (high dark current, slow response) (4-5). Moreover, we develop a strategy to enhance the hybrid material's absorption by coupling it to an optical resonator. Finally, we demonstrate that the final structure has an enhanced absorption of a factor 4 allowing for an 80 K increase of the operating temperature. The resulting device has among the highest intraband-based photodetection performances.

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**Mots-Clés:** Nanocrystals, Infrared, Optoelectronics

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# Self-assembly and poisoning effect on binary ferrofluids of flower-shaped nanoparticles

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Ferrofluids, colloidal solutions of nanoparticles with unique dipolar moments dispersed in water, present fascinating properties due to the magnetic dipole interactions between particles and their ability to move freely in a liquid. These interactions give rise to exotic shapes, from chain-like structures to complex structures. When an external magnetic field is applied, the assemblies turn into microsized chains oriented in the direction of the field, which modify the magnetic properties of the fluid. Variation of the nanoparticle size, shape and composition (e.g., hard or soft magnetic material) changes the magnetic anisotropy, which plays a crucial role in magnetic dipole interactions. This results in a modification of the structuring of ferrofluids as well as their collective magnetic properties like coercivity, magnetic saturation or remanence. Magnetic binary ferrofluids, i.e. those composed of two types of nanoparticles with different magnetic anisotropy, are particularly appealing because they offer an unprecedented interplay of magnetic dipole interactions. Understanding and controlling interparticle interactions could lead to improving the efficiency of known ferrofluids for applications in the biomedical industry and the discovery of novel magnetic responsive materials.

We investigated the relationship between self-assembly and magnetic properties at several scale. Bulk magnetometry (SQUID and FORC) reveal the macroscopic magnetic properties of the ferrofluid. On binary ferrofluids mixing a hard and a soft magnetic material, chemically selective magnetisation curves were measured by Resonant Inelastic X-ray Scattering spectroscopy combined with X-ray Magnetic Circular Dichroism with hard x-rays. We show that the magnetic properties of the binary ferrofluid is not the average of both components and that a soft magnetic material harden under the influence of a hard magnetic material. At the microscopic and nanoscale, we use Cryogenic Transmission Electron to image the self-assembly of the ferrofluid, and Electron Holography to measure the magnetic induction inside an assembly of nanoparticles.

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**Mots-Clés:** magnetic nanoparticles, ferrofluids, microscopy, magnetometry

# Enzyme-assisted mineralization of calcium phosphates: role of collagenous and non-collagenous proteins.

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Calcium phosphate (CaP) mineralization is a process to build hard tissues for vertebrates such as bones or teeth. In vivo, the formation of CaP mineral involves a combination of physico-chemical and biochemical processes and takes place in a complex extracellular space containing various biomacromolecules and in particular proteins, that be divided between collagenous and non-collagenous proteins. The mechanism by which biomolecules are involved in the mineralization process is still not completely understood. The formation of CaP minerals has been the subject of vast literature describing the thermodynamics and kinetics of the process in abiotic systems: in aqueous media without taking into account the intricacy of biological systems. In this work, we aimed to explore an advanced biomimetic system mimicking *in vivo* CaP mineralization. The development of a biomimetic system, which allows a thorough investigation of the CaP mineralization process, requires coping with the complexity of the biological environment. This includes homeostasis processes and compartmentalization, which keep constant key physiological factors and enhance the efficiency of the biological process. To include the key features, we combined three key strategies; (i) enzyme-assisted mineralization, (ii) the self-assembly of biomacromolecules at solid surfaces and (iii) the heterogenous nucleation to mimic the in vivo CaP mineralization. Then the mineralization process was monitored from the early stages in real time.

**Mots-Clés:** Biomineralization, calcium phosphate, enzyme, collagen

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# Application of biosurfactant-modified montmorillonite as viscosity enhancer for vegetable-oil-based drilling fluids

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The application of organic montmorillonite as an additive in oil-based drilling fluids has long been a subject of research. Inspired by zinc soaps in paints, an organoclay modified with zinc ions and lecithin was synthesized and dispersed in the organic phase of vegetable oil-based drilling fluids. The thixotropy and the viscoelasticity of drilling fluids were examined and six rheological models were employed to match the fluid parameters quantitatively. It was observed that the thixotropy of drilling fluid increased as the temperature increased from 60 to 120○C, followed by a decrease as the temperature raised from 120 to 180○C. The drilling fluid behave as a non-Newtonian fluid exhibiting good shear thinning with a viscoelastic gel structure at temperatures below 120○C. As the temperature further increases, the drilling fluid behaves as a Newtonian fluid due to the degradation of the organoclay and the breakdown of the gel structure. The Herschel–Bulkley and Tscheuschner model outperformed the other models in simulating fluid rheological behavior. The XRD and TEM results demonstrate that the exfoliation of organic Mt is the main reason for the increase of oil viscosity and thixotropy, but too high temperature will lead to the degradation of organoclay, which in turn leads to poor rheology. The prepared organic montmorillonite presents a potential for use as an additive in the oil-based drilling fluid at appropriate temperature.

**Mots-Clés:** montmorillonite, drilling fluids, linseed oil, rheology, exfoliation

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# Polyethylene nanocomposite with self-healing properties for vehicle applications

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Over the past several years, car manufacturer have been commited to reducing the environmental footprint of their production systems and vehicles. Plastics, representing more than 250kg of the vehicle mass, are suitable for many applications and for reasonable costs, they can meet some of the consumer expectations, as well as European directives. However, although theoretically recyclable for thermoplastics or upgradeable for thermosets, their integration into recycling channels is an issue as the different constituents can not be easily separated.

Therefore, making plastics with self-healing property would increase there lifetime and by extention, the reparability of vehicles. Dynamic materials, such as ionomer or new vitrimer-type materials, are one of the possible key to meet this need. They contain reversible bonds that can be broken and reformed under a certain stimuli inducing properties such as shape memory, self-healing or mechanical energy dissipation.

For automotive industry, polyolefins are the most widely used polymers (60% of plastic materials). Therefore, this project aims to create permanent 3D networks with self-healing properties, as shown in Fig. 1. By introducing inorganic particles fonctionnalized with dynamic ionic bonds in high density polyethylene, it was found that chains were reversibly crosslinked at the organic-inorganic interface providing scratch healing ability by thermal stimulation, while maintaining the material shape and intrinsic properties such as Young's modulus, ultimate tensile strenght and cristallinity.

**Mots-Clés:** Self, heling, hybrid polymer, ionomer, dynamic crosslink

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# Anionic ring-opening copolymerization of epoxides and thiolactones : a way to synthesize recyclable poly(ester)s

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Poly(ester)s are among the most commonly used plastics in the world, for examplein the textile industry. More than 300 millions tons of plastic are produced every year, causing dramatic and global environmental issues and it is urgently necessary to develop more sustainable production processes that are more compatible with a circular and sustainable economy. Since 2019, a new synthetic route toward poly(ester)s has been developed in our laboratory by the alternating copolymerization of epoxides and thiolactones through an anionic polymerization process.1 This polymerization leads to the formation of well-defined poly(esterthioether)s. This versatile polymerization method has already been used to obtain a wide range of structures by varying the monomer structures. We were able to polymerize biobased monomers such as N-Acetyl Homocysteine Thiolactonce and eugenol-derived epoxides, forming fully biobased polymers. Solventless polymerization methods were also tried with positive results, therefore enhancing the green nature of our method. 2,3

We are currently interested in the recyclability of our poly(esterthioether)s by studying their depolymerization and their repolymerization. It was established that these alternating copolymers can be totally depolymerized in basic or acidic medium, resulting in the recovery of the repeating unit. This unit can actually be used as an AB monomer for bulk polycondensation and reform the native poly(ester-thioether) (Figure 1). Moreover, studies are currently underway to evaluate the cyclability of this recycling process.

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# Ferritin nanocages used as programmable bricks for biomolecular electronics

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A long-standing goal in biomolecular electronics is the development of a reliable approach for integrating proteins and peptides into electrical circuits. Compared with synthetic molecules often studied in molecular electronics, proteins are much larger and also exhibit a very reproducible structure. Ferritin is an iron cellular storage protein present in many living bodies. It is made of a self-assembly of 24 polypeptides (amino-acids chain) in a highly symmetrical structure with a 12 nm diameter (Fig.1). Part of ferritin is to handle di-iron ions (Fe2+) via an oxido-reduction reaction to form a ferrihydrite (Fe2O3H20) core that contains up to 4800 iron atoms. Due to its unique architecture, ferritin has strong assets to be used in electronics devices. In this project we propose a strategy to assemble, and characterize a biomolecular active layer based on ferritin nanocages. While the native ferritin has a negative surface charge at neutral pH, bioengineering of the ferritin is realized to change its surface charge to positive. Then, ferritin nanocages monolayer is deposited on a doped silicon wafer and its global charge can be programmed by adjusting the ratio of positively vs. negatively charged ferritins. The morphology and the nanoscale electrical properties of this monolayer is investigate using a Kelvin Probe Force Microscope (KPFM). As proof of concept, a ferritin monolayer is deposited on a fully-depleted transistor and studied to gain supplemental insight into the dynamic and time-resolved electrical behavior of the monolayer.

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# Molecular motions of statistical copolymers at the interfaces with silica particles

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Polymer-based composites with silica particles are an important class of materials. In these systems, an improvement of some of the mechanical properties such as the elastic modulus compared to the neat polymer matrix may occur. The dynamics of polymer chains at the interfaces with the filler particles are one of the mechanisms responsible for this enhancement as shown in recent works on homopolymer-based nanocomposites (1). Although statistical copolymers are good candidates as compatibilizing agents, there are only few theoretical studies on nanocomposites composed of statistical copolymers focusing on the influence of two types of units, hydrophilic and hydrophobic ones, on the nanocomposite mechanical behavior (2). From an experimental point of view, this question remains to be adressed.

The aim of this work is to describe the local properties of polymer chains at the organic-inorganic interfaces of nanocomposites based on silica nanoparticles and poly(ethylene glycol-*ran*-propylene glycol), P(EG-*ran*-PG), which is composed of hydrophobic units (PG) and hydrophilic units (EG). This description includes the nanocomposite microstructure, the local concentration of PG and EG units as a function of the distance with the nanoparticle surface and also the dynamical behavior of chain segments at the interfaces. The long-term goal of this project is to find some links between these information, obtained at the local length scale, and the mechanical behavior of these nanocomposites.

SAXS experiments indicate a similar polymer/silica microstructure for both PEG and P(EG-*ran*-PG)-based nanocomposites. 1H and 13C solid-state NMR experiments evidence the occurrence of a "glassy" layer (3), including immobilized copolymer chain segments, at the interfaces. Moreover, the presence of PG hydrophobic units seems to slow down the reorientational motions of EG units which translates an increase of the interactions between silica nanoparticles and the copolymer chain segments.

**Mots-Clés:** nanocomposites, statistical copolymers, silica nanoparticles, molecular motions, interfaces

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# Doping strategies to unlock the anionic redox of Li-rich titanium chalcogenides

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Capacity of commercialized cathode materials for Li-ion batteries is restricted by the stoichiometry of the compounds, with a ration Li by transition metal (TM) lower or equal to 1. To increase the reachable capacity, Li-rich layered oxides, namely Li1+xTM1-xO2, were successfully synthesized last decades, improving the capacity from around 180 mAh/g to 250 mAh/g. However, this gain of capacity is undermined by detrimental phenomena as voltage fade or capacity decrease along cycling.

My research subject is the synthesis of Li-rich chalcogenides which can reach the same capacities as oxides, without the drawback occurring during cycling, thanks to their higher covalency between the TM and the anions. Li2TiS3 is the starting compound thanks to the low cost of titanium, but by itself, it is electrochemically inactive. Though a doping, either anionic or cationic, unlock the electrochemical behavior of the compounds and effectively enables a sustainable capacity of 230 mAh/g. Manganese, iron or vanadium can be used as cation doper, and selenium is used as anion doper. All of these doping leads to a capacity that can only be explained by the redox couple of the TM together with the anion.

Moreover, 2 phases are mainly obtained during these syntheses depending on the nature of the anion and the doping TM : $R$-3$m$ (O3) or $P$-3$m$1 (O1). In certain circumstances, the pristine O3 can shift to an O1 structure upon Li removal. This discovered phase transition is currently undescribed in the literature and is tried to be rationalized through this work thanks to the variety of composition obtained.

**Mots-Clés:** Li, ion battery, anionic redox, sulfide synthesis, doping

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# Design of Nanoparticles with Novel Compositions and Monitoring of their Electronic Properties for Applications in Nanomedicine

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Nanoparticles (NPs) in which magnetic and optical properties coexist have been explored intensively for diverse biomedical applications including diagnostic, in vivo imaging and therapy. Semiconductors are key components for their unique features, photoluminescence properties, electronic properties, tunable size and high photostability. Gadolinium oxysulfide (Gd2O2S) nanoparticles are promising candidates for biotechnologies as they have been used as MRI contrast agent or X-ray absorbing materials. When doped with cerium, they gain an additional functionality as visible light absorber due to the decrease in the material bandgap from 4.7 to 2.1 eV. Further biomedical applications may be envisioned thanks to the combined antioxidant properties of cerium and the magnetic properties of gadolinium. Understanding the molecular-level interactions between organisms and nanoparticles to guide and enable the design of novel materials that are less toxic remains a challenge. In order to understand these interactions at the nanoscale, we study the change in the physico-chemical properties of the NPs when they are immersed in a biological medium. In an environmental matrix, pristine nanomaterials transform and acquire a corona of biomolecules, such as proteins, which can sheild the identity of a nanoparticle. This is known as the nano-bio interface. We developed a process where the nanoparticles are obtained via a colloidal synthesis under inert atmosphere, then they are dispersed in an optimized mix of solvents and deposed onto a substrate thanks to dip coating. As a result, we have access to the bare surface of the nanoparticles, which was very complicated before (e.g. in solution). The nanoparticles properties are now ready to be monitored before and after immersion in different electrolytes. The characterization techniques include spectroscopic ellipsometry, XRD, SEM-FEG, cyclovoltammetry. Results will be helpful for harnessing the protein corona towards safer by design nanoparticles.

**Mots-Clés:** nanoparticles nano, bio interface

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# Biomimetic collagen tubular scaffolds for vascular applications

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Pathologies such as phlebitis, stroke, arteriopathy or pulmonary embolism originate from blood vessel occlusion. Currently, to address these clinical issues we rely on synthetic arterial grafts, but their use to replace small diameter vessels leads to recurrence of the occlusion. To tackle this limitation, radically new materials are necessary, that combine a porous tubular structure and a native-like composition. These characteristics should favor cell infiltration, device biointegration and lead to mechanical performances similar to those of native arteries.
Here, we propose a method that enables to recreate the above-mentioned properties using the main protein found in the arterial wall, type I collagen. Control over the macro and mesostructure of the collagen materials, respectively the tubular shape and the porous network, is achieved using ice-templating. At the nanoscale, we recapitulate the native tissue fibrillar motifs of collagen through topotactic fibrillogenesis, a process introduced by our team earlier1,2.

Control over the ice growth kinetics allowed to tailor the mesostruture of the tubular materials. Fine-tuning spatial pore distribution leads to pore sizes ranging from 20 to 130 $\mu$m, and generates an interface similar to that of arterial layer junctions. This strategy allowed to reach high local collagen concentration (100-200 mg/mL), propelling this material as the first substitute reaching the range of native tissues. These characteristics resulted in facilitated cell diffusion and proliferation rates (human umbilical endothelial cells and smooth muscle cells), and on mechanical properties (elongation, storage modulus) in line with those of arteries3.

The materials fabricated with our approach are currently assessed for vascular applications *in vivo*, and will be extended to tracheal replacement.

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3. Martinier *et al. in prep.*

**Mots-Clés:** collagen, vascular, biomimetism, biomaterial

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# Workflows for detecting cross talks for Ni rich coumpounds in Li-ion batteries

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To quickly screen high energy density intercalation compounds or more stable electrolytes for Li-ion batteries, metrics such as capacity retention or coulombic efficiency are often used. These metrics are efficient at assessing initial degradation of the battery performance. Nevertheless, more than the linear degradation of battery performance with time, the battery lifetime is often regulated by the appearance of the so-called "knee points" in capacity retention. Knee points are the indication of a change of degradation mechanism or associated rate and are often followed by capacity rollover, during which the capacity retention abruptly degrades to lead to the sudden death of the battery cell. Capturing complex chemical and mechanical events which when cascading lead to capacity rollover is challenging, especially for cross talking mechanisms during which degradations at one electrode directly disrupts the functioning of the second one. Indeed, cross talking events often happen simultaneously to "classical" degradation modes occurring at sole electrode such as impedance raise, higher lithium loss inventory and loss of active material, complexifying their detection. In this work, Ni-rich layered compounds were studied, LiNiO2 and LiNi0.8Mn0.1Co0.1O2, in full cell configurations. By varying the electrolyte chemistry and the cycling conditions (cutoff potential and temperature), cross talking mechanisms are pinpointed by the introduction of dedicated protocol workflows combining derivatives curves (dV/dQ & dQ/dV) and charge/discharge capacity endpoints. Applying these workflows to graphite/NMC811 chemistry using 5M LiFSI in DMC electrolyte, we demonstrate that super concentrated DMC-based electrolytes are plagued by cross-talking events, albeit good capacity retention is recorded in full cell. Furthermore, we show that SEI formation at high temperature ($>$ 55oC) is efficient to alleviate cross-talking phenomena. Overall, we propose novel workflows for detecting complex mechanisms. We believe that their implementation is of prime importance to go beyond our understanding of classical aging mechanisms.

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# Reactive processing of polyesters to form vitrimers with dioxaborolane metathesis as the exchange chemistry

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**Abstract**

Introduced in 2011 by Montarnal et al (1), vitrimers are a specific class of material: they are networks with dynamics bonds, which give them specific properties, such as insolubility, reprocessability, and possible self-healing and compatibilization between materials. Several dynamic chemistries can be used in vitrimers. Among these, we will focus on boronic ester metathesis, developed in 2017 by Röttger *et al* (2) dioxaborolane metathesis presents several advantages: the exchange can take place at room temperature and without a catalyst, and, more importantly, it has already been implemented in thermoplastics.

With recycling in mind, it is interesting to implement vitrimers in different thermoplastics. Polyesters are a target of choice, as they are very common single-use plastics. The goal of this project is to synthetize vitrimers starting from polyesters (PET, PLA and PETg) using boronic ester metathesis as the exchange chemistry.

The synthetic pathway chosen to synthesize vitrimers relying on dioxaborolane chemistry has two main steps: First, dioxaborolanes are introduced into the polymer chain by transesterification, then the modified polymer is crosslinked with a molecule containing three or more function which can react with alcohol.

During the first two years, this approach has been tried on PETg and PLA. Two dioxaborolanes, a small difunctional molecule and a multifunctional oligomer, were synthesized and tested for the synthesis of vitrimers. Different coupling agents, such as a poly(styrene-co-maleic anhydride) oligomer, pyromellitic dianhydride (PMDA), and diglycidyl ether of bisphenol A (DGEBA) were also used as chain extenders in the crosslinking step. So far, the most promising results had been obtained using a difunctional boronic ester in conjunction with DGEBA.

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2. Röttger, M. *et al.* High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **356**, 62–65 (2017).

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**Mots-Clés:** Vitrimers, polyesters, recycling, boronic ester

# Hybrid Organic-Inorganic membrane as new Electrolyte in All Solid-State Battery

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All-solid-state lithium batteries are considered like the next generation of electrochemical energy storage devices because of their safety and their high energy density up to 400Wh/kg. The all-solid-state battery is composed of a solid electrolyte, which is the critical component, composed of inorganic and/or solid polymer electrolyte (SPE). SPE can be easily shaped and their flexibility allows obtaining a good interface with the electrode materials. Inorganic compounds generally have high ionic conductivity (10-3S/cm), they are stable electrochemically vs Li/Li+ and their transport number is close to 1. To combine the advantages of both types of materials, hybrid materials have been designed. First, the optimization of the polymer matrix has been performed. A solvent-free synthesis has been designed from liquid and commercial precursors Poly(ethylene glycol)-methyl-methacrylate-(PEGM) and Poly(ethylene glycol)-dimethacrylate-(PEGDM). These latter are copolymerized with Lithium-3-((trifluoromethane)sulfonamidosulfonyl)-propyl-methacrylate-(MTFSLi). The anion TFSI- is thus grafted to the PEO network, allowing exclusively the diffusion of the Li+ ion, and the polymer matrix can be classified as single-ion conductor. The ratio PEGDM:PEGM can be easily tuned. This parameter affects the cross-linking density which modifies the storage modulus (E') and therefore the free volume, the glass transition temperature (Tg) and consequently the ionic conductivity which are the main properties required for SPE. Finally, a ratio of PEGM:PEGDM (80:20) was selected because the obtained homogeneous SPE is self-standing and soft @25◦C, amorphous with a Tg of -41◦C. The EO/Li ratio was then modulated. Finally, an optimum in ionic conductivity of 2.10-7 S/cm @25◦C has been found for EO/Li ratio of about 20. The transport number measured by the Bruce-and-Vincent method is t+=1, demonstrating the good grafting of the TFS-. Moreover, the electrochemical stability of this single ion system extends from 0 to 7V vs Li+/Li. Once the polymer matrix is optimized, the hybrid materials including Li6.4La3Zr2Al0.2O12 (LLZO) will be synthesized.

**Mots-Clés:** All solid state batteries, hybrid, electrolyte

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# Topological defects in smectic liquid crystal thin films

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The study of topological defects has been of interest for over a century since they are structures that can be found from cosmology to biology and condensed matter. However, their intimate structure still usually remains elusive. In this context confined smectic liquid crystal thin films that can lead to the formation of topological defects (1) are useful since they allow for the use of X-ray scattering to study the defects at an unprecedented resolution.
Using Grazing Incident Small-Angle X-ray Scattering (GISAXS) on the SIXS beamline of Soleil Synchrotron facility, we studied the internal structure of an array of oriented smectic topological defects in thin smectic-A liquid crystal films (thickness = 180nm) of 4-n-octyl-4'-cyanobiphenyl (8CB) confined between two strong antagonistic anchoring imposed by Polyvinyl alcohol substrate (planar unidirectional) and air (homotropic). These films are made of smectic layers superimposed in flattened hemicylinders . X-ray scattered Bragg intensity I($\alpha$) is proportional to the number, n($\alpha$), of smectic layers, whose normal, parallel to the wave-vector transfer, q, makes an angle $\alpha$ with the substrate (2). The precise determination of Bragg intensity when $\alpha$

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varies from 0◦ (perpendicular layers) to 90◦ (horizontal layers) has been possible through the combined theoretical and experimental determination of the corresponding sample orientation for each $\alpha$.

The observed variation of this intensity as a function of $\alpha$ allowed to reconstruct the superimposed rotating smectic layers of each quarter of cylinder of one given flattened smectic hemicylinder. We evidenced with a nanoscale precision 3 types of topological defects included in one given smectic hemicylinder, all oriented along a single direction parallel to the hemicylinder axis: 2 dislocations, 1 disclination with a core of size around 10 nm per micrometer together with a 2D ribbon-like topological.

**Mots-Clés:** Smectic Liquid crystal, Topological defects, GISAXS

# SYNTHESIS OF POLYCATIONIC VECTORS FOR GENE DELIVERY

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Gene therapy consists in the insertion of genetic material (DNA or RNA) into cells to modulate their functioning (1). A vector is needed in order to protect the genetic material and to target the right cells. Viruses were first considered (2) for their great transfection efficiency, but their biological drawbacks (size, immunogenicity) and their high production cost opened the way to synthetic alternatives such as polymeric (neutral or polycationic) and lipidic vectors (3). Despite a decrease in transfection efficiency, these synthetic vectors, such as polymers, have many advantages. The size of the polymer is controlled, chemical functions can be grafted to facilitate the targeting of certain cells in the organism and their toxicity is greatly reduced.

In this project, we develop new triblock copolymers for gene delivery from different oxazoline-based monomers. One of these blocks will be hydrolyzed into a cationic block to condensate the DNA *via* electrostatic interactions, the other one will bring cohesion to the system and the last one will bring steathlness to the vector. The objective is to form polyplexes (complexes made of DNA and polycation) and to test their transfection efficiency on cells first, then developing their delivery by nebulization.

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**Mots-Clés:** Polymer, DNA, Gene Therapy, Synthetic Vectors

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# Formation of chiral helices by self-assembling molecules on semiconductor nanosubstrates

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Among semiconductor colloidal nanocrystals, 2D nanoplatelets (NPLs) are geometrically seen as well-defined flexible substrates for the self-assembly of molecules. In the presence of mechanical stress brought by surface stabilizers, helical structures are formed according to the parameters of the initial material after internal energy relaxation.

Here, we demonstrate the tuning of the NPLs helices radii through the organic ligands, described as an anchoring group and an aliphatic chain of a given length. A perfect control in surface chemistry allows the switch between different morphological features of these nanohelices. Nonetheless, their optical properties in the visible region are well-preserved upon such modifications. Numerical simulations and as well as structural X-ray diffraction studies done on these anisotropic nanoparticles, unveil a strong preferential orientation effect on their resulting scattered patterns.

A mechanical model accounting for the misfit strain between the inorganic core and the organic ligands, enables to predict the nanohelices radii. The model treats these different layers of substrate, anchoring group and aliphatic chain contributions individually and demonstrates good agreement for all studied homo- and hetero-structure cadmium-based NPLs. It reveals ultimately that the self-assembly of surface molecules is equivalent to a layer, whose Young modulus in lateral compression can be estimated close to 0.9 GPa.

Furthermore, the chirality of the semiconductor nanohelices shown in this work is dictated by the ligands anchoring group and can be inverted from one population to another. Chiroptical properties exhibited in circular dichroism measurements show a special interest in investigating this type of mirror-symmetry-breaking particles and could undoubtedly, lead to the emission of circularly polarized light in the visible spectrum.

**Mots-Clés:** Chirality, Mechanics, Nanohelices

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# Synthesis & Functionalization of Hybrid Plasmon-semiconductor Nanoparticles for Cancer Phototherapy

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Clinical modality based on light activation and photosensitizers, phototherapy, has been recognized as a novel alternative for cancer therapy owning to its high selectivity, safety and compatibility with other tumor ablation modalities. However, key challenges such as low light penetration, low generation rate of reactive oxygen species (ROS) for photodynamic therapy (PDT) or of heat for photothermal therapy (PTT), along with poor distribution specificity of photosensitizers have restricted its widespread clinical use, which requires rational design and improvement on photosensitizers. Herein we propose a strategy that combines plasmonic gold nanorods (AuNR), which can efficiently generate hot electrons under laser irradiation thanks to its localized surface plasmon resonance, with semiconductor materials such as TiO2. The generated hot electrons can be injected into the conduction band of TiO2 and eventually produce ROS (·OH), radicals that will lead to cell apoptosis. By controlling the aspect ratio of AuNR, the longitudinal absorption of AuNR can be tuned from 700 to 1000 nm, a region where light gets an optimal penetration into the tissue. We characterized the production of hydroxyl radicals by AuNR/TiO2 nanoparticles under continuous wave or pulsed irradiation at 800 nm by measuring the degradation rate of methylene blue. Then we designed surface polymeric ligands based on polyethylene glycol to ensure the colloidal stability of these hybrid AuNR/TiO2 nanoparticles in a physiological environment. Finally, these functionalized AuNR/TiO2 nanoparticles were incubated with HeLa cells. We demonstrated that irradiation of these nanoparticles by a continuous 808 nm laser was effective to produce ROS and kill cancer cells, while incubation with nanoparticles in the absence of irradiation or irradiation in the absence of the nanoparticles did not modify the cell viability.

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# Development of fluorescent pearls and study of their stability in biological media

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Nexdot is developing a new technology for colloidal semiconductor quantum plates. They're also working on their encapsulation by an aerosol-gel process to protect the quantum plates from ambient humidity and oxygen. One of the possible applications would be the use of these encapsulated quantum plates as probes for in vitro diagnostic tests (IVD). The goal of this project is to develop fluorescent pearls with a controlled surface chemistry to allow coupling with biomolecules. For this purpose, an efficient encapsulation of a plurality of nanoparticles must be developed to optimize their fluorescence quantum yield. The developed capsules should be stable in aqueous solvents used in IVD tests. one of the main challenges is to find the most suitable encapsulating oxide matrix for the stability of the pearls in biological media. different oxide matrix from aluminium to mixed oxide have been tested.

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# Modulation of the Network Connectivity in Vitrimers

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Vitrimers are permanent chemical networks incorporating dynamic covalent bonds that undergo degenerate exchange reactions (1). These exchange reactions allow vitrimers to behave like a viscoelastic liquid under processing conditions, while the associative nature of the exchange mechanisms ensures a constant average crosslinking density across all temperatures (2). Our laboratory recently developed vitrimers relying on boronic ester metathesis that exhibit highly desirable features such as compatibility with polar and apolar polymer matrices, improved thermomechanical properties and adhesion, or healing capacity (3 and 4). Nevertheless, improving the processability remains an important challenge. Indeed, the high viscosity caused by the temperature-independent network connectivity can preclude in some cases the use of typical techniques used in the processing of thermoplastics, such as extrusion and injection molding. To address this issue, we propose to use small molecules to modulate the network connectivity and rheological behavior of vitrimers at high temperatures. Vitrimers with different loads of additive were characterized by dynamic mechanical analysis and rheology, giving insight into the complexities of this system. This approach is an innovative and promising way to improve processability of vitrimers and render them more industrially interesting as a promising next-generation material for recycling and upcycling applications.

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**Mots-Clés:** Vitrimers, dynamic covalent chemistry, boronic esters, processability.

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# Mesoporous silica supported Ni catalysts for an optimized production of phenols through lignin hydrogenolysis

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Catalytic hydrogenolysis of lignin is considered as an efficient pathway to produce high-valued aromatic monomers. Among different metals, nickel is a good choice because of its rather low cost and abundance. However, the hydrogenolysis of lignin by Ni-based catalysts is limited by the competitive hydrogenation of aromatic rings. In our work, such hydrogenation has been minimized with the use of an H-donor solvent instead of dihydorgen as well as Ni/Fe or Ni/Co silica-supported alloys. Re-polymerization giving rise to more recalcitrant lignin should also be avoided. Presently, we are investigating, in a very systematic manner, how silica porous supports can limit re-polymerization as a result of the physical separation of lignin molecules. First of all, highly active, well dispersed, and stable ultra-small zero-valent metal nanoparticles were required. For our preliminary tests, impregnation of commercial silica by Ni(II) with or without additional metals in the presence of ammonia was used and the conditions modified to improve Ni activity. For the other part, mesoporous silicas with tunable pores sizes and/or structures, embedding Ni nanoparticles are considered. Targeted products are phenols which are extremely interesting as building blocks of new synthetic bioplastics, phenol-formaldehyde resins or epoxy- or polyurethane materials. The challenge is to convert polymeric lignin into simple phenols in high yield.

**Mots-Clés:** lignin, nickel, silica, depolymerization, repolymerization, mesoporosity

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# Ultra-stretchable smart hybrid hydrogels: nanoplatelets/cubosomes as physical cross-linkers

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We are aiming at developing a new external drug delivery-based application such as artificial skins and/or smart bandages by trapping an active substance to be released upon stretching. We design hybrid physical hydrogels by combining two systems that attracted a lot of attention lately, aiming to get the best of both: (i) aqueous dispersions of lipid-based lyotropic liquid crystalline phases stabilized in water by nanoparticles (NPs), (ii) hydrogels physically cross-linked by NPs that have shown exceptional mechanical properties.

Herein, we use Phytantriol (PT) as a lipid, a skincare product that forms bicontinuous cubic phases in excess water at ambient temperature. This bulk phase is mechanically broken in the presence of Laponite nanoplatelets that stabilize the LC phase in finite domains without disturbing it. We varied both PT and NP concentrations in order to optimize the structure of these LC/NP dispersions for our final purpose. The dispersions were characterized via a multi-experimental approach, including small-angle x-ray and neutron scattering, conductimetry and dynamic light scattering, allowing a comprehensive multiscale understanding of the materials.

Polyacrylamide-based hydrogels were synthetized by free radical polymerization directly into the LC/NP dispersions, which act as purely physical cross-linkers. We implemented two different protocols with adding acrylamide monomers as i) the last synthesis component and ii) the first synthesis component. Impressively, in both cases the final hydrogels could be stretched up to 1000% without breaking. Their structure was characterized *in situ* at rest and under uniaxial stretching by small angle neutron scattering. The results reveal that the deformation of the LC/NP cross-linkers mainly depends on the hydrogel synthesis approach while the LC/NP pristine dispersion mainly influences the final hydrogel ultra-deformation properties.

**Mots-Clés:** Lipids, Cubosomes, Nanoplatelets, Cross, linkers, Hydrogels

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# Activity enhancement of CoP nanocatalyst by decoration with phosphines for alkyne hydrogenation

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Most of human's needs in energy, chemicals and materials still rely on fossil non-renewable feedstocks. Meanwhile, the scale of human activities threatens the balance of biogeochemical cycles of elements such as carbon, nitrogen and sulfur: COx, NOx and SOx are released in colossal amounts as wastes. Their accumulation in the atmosphere is responsible for global warming as well as ocean acidification. From the chemist's point of view, their valorisation requires an activation or a reduction step to elongate or break the strong bonds of these stable small molecules. Dihydrogen, as a reducing agent, similarly needs to be activated to become reactive. This paradigm shift provides a new feedstock of building blocks to conduct atom-economical reactions.

Activation and reduction of small molecules under mild conditions is a challenge and requires fine design of catalysts. Such a breakthrough was exemplified fifteen years ago by Frustrated Lewis Pairs (FLP) for dihydrogen heterolytic cleavage at room temperature. FLP are composed of bulky strong Lewis acid and base, typically tertiary boranes and phosphines, prevented to form an adduct because of their steric hindrance. Our research aims at extending the scope of such homogeneous catalysts by substituting one of the molecular partners by acidic or basic nanoparticles. The presented results focus on the activation of dihydrogen by colloidally synthesized cobalt phosphide nano-urchins. By addition of tri-n-butylphosphine, we highlighted a strong enhancement of their catalytic activity at low temperature for a model hydrogenation reaction. Careful *post-mortem* study of the catalyst evidenced the absence of active molecular species.

In addition to base screening and mechanistic studies carried out, a deeper understanding of the catalytic active site at the interface between the metallic surface and the molecular base needs to be provided with computational studies and under going *in operando* characterizations.

**Mots-Clés:** Nanocatalysis, Small molecule activation, Hydrogenation, Metal phosphide nanoparticles

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# Bio-Inspired synthesis of coloured CaCO3 through the incorporation of naphthoquinones within ACC phase

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Skeletal elements of sea urchins, especially their biomineralized spines show intense colors due to the presence of polyhydroxylated naphthoquinone (PHNQ) molecules.1 PHNQ molecules have low stability towards sunlight and pH variations but exhibit resistance when incorporated into the biogenic calcite resulting in colorful organic-inorganic hybrid crystals.2 In sea urchins, biomineralization pathways occur via the assembly of amorphous calcium carbonate (ACC) nanoparticles that further crystallize into calcite.3,4 Some organic molecules were shown to control in vitro ACC stability and crystallization as well as crystal morphologies and structure.5,6 However, the role of organic pigments during ACC formation and crystallization is poorly understood although it was suggested that pigmentation and biomineralization processes in sea urchins might be coupled.7 To better understand the role of organic pigments in biomineralization we performed bioinspired synthesis of ACCs in the presence of naphthazarin molecules and study their spontaneous crystallization in water. Here, we present our results for the synthesis of ACC by the addition of CaCl2 to a Na2CO3 solution8 in the presence of naphthazarin . Pair distribution function analysis evidenced that the presence of pigment does not affect the local structure of the ACC. However, by monitoring pH and Ca2+ ions concentration during the reaction and performing XRD at different times, we showed that the presence of pigment retards the crystallization of ACC which transforms into a mixture of calcite and vaterite that further converts to calcite only. The blue calcite crystals conserve their color after bleaching experiments whereas the ACC particles do not, suggesting that pigment incorporates during ACC crystallization. Indeed, ss-NMR shows organic-inorganic interactions in the hybrid crystalline pigment and HR-XRD gives insights into the pigment inclusion mechanism.

**Mots-Clés:** Biomineralization, Naphthoquinones

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# First alteration step of flat glass surface in the atmosphere: role of glass composition

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The surface of flat glass reacts with the atmosphere as soon as it is formed, which can lead to quality issues. The atmospheric alteration of glass refers to specific ageing conditions in unsaturated humidity (Relative Humidity, RH $<$ 100 %). The involved mechanisms are different from those of the most studied alteration, which is in immersion conditions, with liquid water (1). Indeed, the alkali and alkaline-earth cations released from the alteration reactions cannot diffuse away. Thus, they stay on the surface or in the alteration layer of the glass. They can lead to the formation of alteration salts on the surface by reacting with atmospheric gases.
Together with the temperature and RH, glass composition is a main factor controlling the alteration (2). Industrial glasses having five different compositions have been studied, before and after ageing. The samples were altered in climatic chamber at 35○C and 80 %RH for 14 days, 28 days and 3 months.

In my thesis, I focused on the first alteration step, happening at the nanometric scale. Therefore, a specific methodology was developed. The approach implemented consists in analysing the alteration salts and measuring the composition and hydration of the glass extreme surface at different stages of the ageing process. Then we looked for a correlation between this evolution and the nature of the glass matrix. The main analytical tools were atomic force microscopy (AFM), attenuated total reflectance infrared spectroscopy (ATR-IR), and secondary-ion mass spectroscopy (ToF-SIMS). We obtained a very good coherence between the different techniques and a relation between the composition parameters and the observed alteration.

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**Mots-Clés:** Flat glass, atmospheric alteration, glass composition, durability

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# Tunable Plasmonic Substrate for LSPR Biosensing

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The PhD project aims to fabricate a tunable and reliable plasmonic substrate for LSPR biosensing. In this work, we chose the bottom-up approach considering its convenience and cheapness. First, colloidal hollow Au nanoparticles (HAuNPs) were synthesized by a wet chemistry protocol. Then, the refractive index sensitivity (RIS) and figure of merit (FOM) of HAuNPs were experimentally and theoretically investigated to optimize the sensing performance of the plasmonic substrate. The optimal colloid was immobilized on a transparent glass slide by a chemistry method. The deposition of HAuNPs on the glass surface was confirmed by scanning electron microscopy (SEM). The extinction spectra of the glass substrate were measured by UV-Vis spectroscopy, showing an intense plasmon band in the visible light range. Band shifts with changes in refractive index (RI) were also documented, demonstrating the qualification as LSPR sensor chips. The drop in RIS after immobilization could be largely offset by avoiding using mixed chemical bonds and reducing the density of the functionalization layer. As a comparison, glass sensor chips using solid Au nanoparticles (AuNPs) were prepared and their optical properties were measured. Our data proved that HAuNPs outperformed their solid counterparts in the RIS and FOM, demonstrating the high potential of HauNPs for LSPR biosensing. In the last part of the project, these nanostructured plasmonic platforms will be used for multiple applications strategizing by biosensing of toxins and water contaminants. The readout will be achieved using a UV-Vis spectrometer with the aim of an application for smartphone readout.

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# A NEGATIVE BASED TIO2 ELECTRODE FOR AQUEOUS PROTON BATTERIES

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Facing the growing need for energy demand, complementary solutions to Li-ion batteries are being studied. In our case, we are interested in a lamellar negative electrode material of TiO2 capable of reversibly intercalating proton-ions for aqueous batteries. One of the main challenges with these batteries come from the low potential window available. With a thermodynamic working potential of only 1.23V, aqueous batteries cannot provide sufficient energy density. Focusing on a material point of view, we believe that optimizing the intrinsic transport properties of proton-ions can lead to the reduction of side reactions such as Hydrogen Evolution Reaction (HER). TiO2, lepidocrocite type, organizes in sheets and has water in the inter-lamellar spaces. It is within this inter-lamellar that proton conduction by the Grotthus mechanism(1) will take place. To allow this initially insulating material to become conductive, different cations can be inserted during the hydrothermal synthesis, thus allowing the reorganization of water molecules that facilitating the intercalation, conduction and diffusion of protons(2). This is what we will show with Zn2+ which has a positive impact on the electrochemical response of the material. Several levels of Zn2+ were tested: from 10 to 50 mol% relative to Ti4+. The electrochemical properties of these materials (shaped with carbon black as conductive support and Nafion as binder) were studied in half-cell aqueous electrolyte buffered at pH 5 (CH3COOH/CH3COOK, pka = 4.76, (1M)). Experimental capacities of more than 100 mAh/g, 80% of coulombic efficiency over 100 cycles have been obtained and potentials down to -1.4V have been achieved, pushing back the phenomena of HER. The performance of these materials will be linked to their physicochemical characteristics, obtained by a panel of techniques adapted to amorphous materials.

**Mots-Clés:** HER, Aqueous battery

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# Study the colors of stained glass to understand the speciation of manganese in glass

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This presentation presents the study of a 12th century Trojan panel currently under restoration at the Manufacture Vincent Petit. This panel is exceptional because of its state of preservation and the shade of purple colors it contains.

Our study will present the results of optical absorption spectroscopy performed with a portable device as well as the synthesis of model glass to better understand the origin of the diversity of colors related to the manganese present on this panel.

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# Development of dynamic nanocomposite polymer by reactive extrusion for and applied in 3D printing to reach in homogeneous mechanical properties

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3D printing is a manufacturing process that enables the conversion of computer design into tangible 3D object by a layer-by-layer printing. One of the main drawbacks of this technique is the induced anisotropy of the mechanical properties caused by the weak interlayer bonds between printed layers. Covalent adaptable networks (CAN) are polymers bonded with reversible covalent crosslinkers. Vitrimer is a new class of polymer among the CAN polymers in which crosslinking between the covalent network is reversible owing to an associative mechanism bond exchange. The network thus behaves like a thermoset/elastomer at room temperature but like a thermoplastic at higher temperature. This presentation will highlight a reversible metal-ligand bond nanocomposite EVA system, a polyethylene vinyl acetate copolymer crosslinked with titanium-oxo-alcoxo precursor. Thanks to reversible transesterification reaction at the crosslinking point, these new nanocomposite polymers lead to 3D permanent network with a vitrimer behavior. First, this presentation will focus on the synthesis of the vitrimer by reactive extrusion and then on the 3D printing of the extruded material with Fused Deposition Modeling (FDM) technique. The process parameters for reactive extrusion and 3D printing had been adjusted in order to obtain materials with vitrimer properties proved by characterizations such as crosslinking degree, TGA, rheology, and gel content. Moreover, we will demonstrate that such dynamic polymer nanocomposites reinforce the interlayer bonds between two printed layers thanks to the introduced reversible bonds that are activated by with the rise of temperature. Following an associative mechanism, there is no loss of the dimensional stability upon reheating the printed object. After thermal treatment, tensile test of samples printed in two different directions and adhesion tests between two layers are used to characterize the decrease of mechanical properties anisotropy.

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# Self-organized gain materials for organic solid-state lasers

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Interest in organic electronics has been increasing during the last decades, leading to the production of several devices based on organic semiconductors such as organic light-emitting diodes (OLEDs).(1) In parallel to OLEDs, the development of efficient organic lasers is still a challenge. Such devices are very interesting because they can generate a monochromatic and coherent light. Their structure is composed of a gain material that is responsible for the stimulated emission, coupled with a resonator and an energy source.
It's been years that organic lasers exist from gain materials in solution.(2) Now, the development of new solid-state gain materials gives access to organic laser diodes (OLDs), which are based on the direct conversion of an electric current into laser light. The first evidence of an OLD was recently shown by the group of Prof. Adachi, using an amorphous material based on a pi-conjugated blue-emitting molecule as the gain material.(3) However, this result was obtained only with one example of dye so far, and showed several limitations such as a very short device lifetime. In this context, the development of new efficient gain materials is highly necessary.

In this project, we propose to develop new gain materials based on two strategies. On one hand, we prepared new D-A-D light-emitting liquid crystals in order to benefit from the strong anisotropy and high processability of such materials to enhance light amplification. On the other hand, we developed a set of alternated D-A copolymers able to emit in a large range of emission wavelength in playing with the strength of the D and A units.

**Mots-Clés:** Optical Gain Material, Liquid Crystals, Polymer, Lasers

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# DESIGN OF RECYCLABLE POLYMER NETWORKS AND POLYOLEFIN COMPATIBILIZATION BY REACTIVE PROCESSING

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In 2019, nearly 180 million tonnes of polyethylene (PE) and polypropylene (PP) were produced worldwide, which constitute nearly half of global polymer production. Despite their ubiquity, the recycling of PE and PP remains very challenging. Objects made from PE and PP are difficult to rapidly sort because of the similarity of their chemical structures. Nevertheless, PE and PP are thermodynamically incompatible, and their mutual processing results in coarse phase separation. The weak interface is responsible for the poor mechanical properties of PE-PP blends. Polyolefin compatibilization has thus been the subject of intense research over the last 30 years. Two main approaches have been reported: non-reactive and reactive compatibilization. The former usually consists of using a premade compatibilizer (e.g., a block or random copolymer) to prevent coarsening and strengthen the polymer-polymer interface by interpenetration and stress transfer. The utility of this strategy is unfortunately limited by a combination of high costs and limited scope. The other strategy entails the reactive compatibilization of incompatible polymers by introducing functional groups that act as bridges across the incompatible domains, but this approach is usually constrained by processing challenges and lack of recyclability. In this study, we propose a novel, robust, and versatile approach for the reactive compatibilization of polyolefins. Reactive processing of PE with a safe, azide-based additive yielded a dynamically crosslinked material featuring good recyclability. In the case of PP, $\beta$-scission precludes overall network formation. By *in-situ* reactive processing of a PE-PP blend, a dynamic, recyclable network was also obtained. Gel fraction experiments suggested successful incorporation of PP chains into the PE network. Morphological analyses revealed a lower size and attenuated coarsening of the PP domains, resulting in a significant improvement of the tensile ductility of the blend.

**Mots-Clés:** Polyethylene, polypropylene, compatibilization, blend, recycling, upcycling, reactive processing

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# Heterometallic (MIV/MII) MOFs as a versatile platform for the photocatalytic overall water splitting reaction

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**Abstract:** Hydrogen is considered a serious alternative to fossil energy as it burns without producing any pollutants. Today, more than 90% of the hydrogen produced is from the steam reforming of fossil fuels (known as black hydrogen or grey hydrogen). Hydrogen production by electrolysis of water using electricity generated from renewable energy sources such as solar energy and wind energy is currently the primary source of green hydrogen. Photocatalytic overall water splitting produces hydrogen, converting solar energy into green hydrogen in one step. This simple, low-energy-intensive, and sustainable hydrogen production process can enrich the existing green hydrogen production system and provide more possibilities for green hydrogen production. Metal-organic frameworks (MOFs), also known as porous coordination polymers (CPs), are crystalline solid materials formed by the orderly coordination of metal ions/clusters and organic ligands. Heterometallic metal-organic frameworks (HMOFs) are usually self-assembled by no less than two metals and organic ligands in an ordered synergistic array, and their high crystallinity, high porosity, and multifunctional catalytic sites promote HMOFs as potential candidates for heterogeneous catalysts, especially in the field of photocatalysis. In our quest for the development of MOFs suitable for photocatalytic hydrogen evolution reaction, we synthesized a series of high-valence (Zr, Ce, Hf) heterometallic metal-organic frameworks, in which unique Cu metallo-ligand and Ni metallo-ligand help these MOFs significantly improve the utilization of visible light. In this communication, the highly versatile structure of these heterometallic MOFs will be presented together with the photocatalytic studies that have shown very promising properties (up to 4.26 mmol H2 gcat-1 in 23 h) in overall water splitting under simulated sunlight irradiation.

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# Phototherapeutic nanoMOFs for Antimicrobial Treatment

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Multidrug-resistant microbes have become a serious problem worldwide due to the misuse of antibacterial agents. Photodynamic therapy (PDT) and photothermal therapy (PTT) have been considered promising alternative approaches to replace or combine traditional antimicrobial treatment (1). Moreover, photoacoustic (PA)-guided PTT is motivating the development of precise and effective treatment. However, many photosensitizers show low efficiency of reactive oxygen species (ROS) generation or light heat conversion, low bioavailability, photostability, and high cytotoxicity. Metal-organic frameworks (MOFs) are a group of crystalline coordinating materials based on cations connected through organic linkers ended by complexing groups, which show high potential in the development of new antimicrobial agents, due to their ultra-high surface area, tuned but consistent pore sizes and easy synthesis. We selected iron-based MOF MIL-100(Fe) due to its great biocompatibility and large drug storage space.

Here, we synthesized MIL-100(Fe) nanoparticles through a green and simple procedure (2). Then loaded the IR775 dye into MIL-100(Fe) through post-synthetic encapsulation routes to get a phototherapeutic platform, MIL-100(Fe)@IR775. The loading efficiency is 83.8±0.3 wt%. The drug-releasing analysis indicated that MIL-100(Fe) can strongly stabilize the IR775 with only 2 wt% releasing in 10 days of soaking in pH 5.5 PBS solution. The study of nitrogen adsorption showed that the BET surface area of MIL-100(Fe) only decrease 8% after loading IR775. The evaluation of photothermal conversion ability in solution exhibited that MIL-100(Fe)@IR775 can achieve a reusable PTT effect, without photobleaching like bare IR775. The PA study in solution also showed these composites can become effective contrast agents with the potential for PA-guided PTT.

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**Mots-Clés:** metal organic framework, phototherapy, antimicrobial treatment

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# Creation of heterogeneous chemoenzymatic catalysts based on the use of Metal-Organic Framework for the selective and eco-friendly amination of alcohols

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Amines are essential building blocks for the synthesis of fine chemicals, agrochemicals, pharmaceuticals, dyes and food industries (1). Transaminases (ATAs) have proven to be efficient for the synthesis of important chiral amines from ketones and aldehydes (2). However, the enzymes are known for the harsh working conditions as well as the fragility. Thus, an enduring research interest is to realize the recovery and recycle of enzymes by immobilization or encapsulation to reduce the high cost of enzymes. Metal-Organic Frameworks (MOFs) are emerging coordination hybrid and crystallized materials composed of metal centers and organic ligands whose interest developed rapidly in the past few decades (3). Thanks to the abundant variety of organic ligands and metal clusters, tens thousands of MOFs have been reported.

In the project, we propose to implement a chemoenzymatic "one-pot" process starting from alcohols as initial substrates to produce amines (Scheme 1). In this process, the alcohol will be first oxidized into a carbonyl intermediate in the presence of a chemical catalyst and subsequently transformed into an amine in the presence of an ATAs. Importantly, both chemical catalyst and enzyme will be attached on a same support, a MOF, resulting in a heterogeneous system. This virtuous system will merge efficiency and robustness of the chemical catalyst with the high stereo-, regio-, and chemo- selectivity of enzymes. In addition, it will positively impact amine formation towards green chemistry requirements in several ways.

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**Mots-Clés:** Transaminases, MOFs, oxidation, amination

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# Magnetron sputtering deposition of Ag thin films: microstructural control using the physical parameters of the PVD process

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Magnetron sputtering deposition is a PVD (physical vapor deposition) thin film coating technique that is used for the deposition of a wide variety of materials, including dielectrics, semiconductors and metals. Ag thin films are of particular interest for the glass industry, and are used for the production of ”Low-E” (low emissivity) double glazing windows. These windows contain an Ag film (approximately 12 nm-thick) on one of the internal glass surfaces, which improves their heat insulation properties all while maintaining their transparency towards visible light. Their heat insulation performance can be improved further by using thinner, higher-quality Ag thin films with lower electrical resistance. Current research efforts aim at finding ways of controlling the Ag film growth and their resulting microstructure and properties.

The aim of this PhD project is to understand the impact of different magnetron sputtering deposition parameters on the Ag film growth during deposition. Experimental work is carried out using the MISSTIC setup (Laboratoire Surface du Verre et Interfaces UMR 125) which combines magnetron sputtering deposition with both in situ and real-time measurements. The latter in particular, are performed inside the sputtering chamber and allow for the detection of different stages of the Ag film growth (nucleation - growth - coalescence - percolation - continuous film formation).

One of the parameters that was studied in this project was the addition of O2 gas to the sputtering chamber during deposition. Using real-time electrical film resistance and SDRS (Surface Differential Reflectance Spectroscopy) measurements coupled with in situ XPS (X-Ray Photoelectron spectroscopy) for chemical characterization at the surface, it was possible to identify the key effects of oxygen addition to the chamber on the growth of the Ag film and its resulting properties.

**Mots-Clés:** Thin films, Ag, silver, magnetron sputtering, growth, nanoscience

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# Synthesis and characterization of Borinic vitrimers

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Vitrimers are cross-linked networks that contain dynamic covalent bonds in their matrices. Within these networks, exchange reactions proceeding according to an associative mechanism (1) can take place, thus maintaining a constant number of chemical bonds in the system at any time and temperature while giving the materials a dynamic and reshapable character. Consequently, vitrimers can combine the advantageous properties of thermosets (i.e. mechanical and chemical resistance) and thermoplastics (i.e. malleability and recyclability) (2).
The aim of the aBOVE project is to design and characterize organo- and hydrosoluble vitrimers relying on borinic acid chemistry and to study them in bulk and in solution. This exchange chemistry was selected for its potential to give access to water soluble vitrimers, an area still unexplored, as well as vinyl-based polyelectrolytes and ion conducting vitrimers. In the case of borinato derivatives, i.e. borinic acids complexed with amino alcohols, we also want to explore the possibility to use the labile N–B coordination bond to induce stimuli triggered auto-vitrimerization of functional polymers. If successful, this approach will offer an innovative route to transform thermoplastics into vitrimers, without the need to add crosslinkers, reactive additives or catalyst to induce network formation.

The attractiveness of boron chemistry for the design of innovative dynamic materials has already been demonstrated in the synthesis of vitrimers based on metathesis reactions of dioxaborolanes (ArB(OR)*2*) (2). Due to their assumed hydrolysis stability, borinic acid derivatives could be an interesting alternative to boronic esters.

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**Mots-Clés:** Vitrimers, dynamic covalent chemistry, borinic esters, borinato

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# Exporing interfacial phenomena in solid-state cathode composites

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Although solid state systems hold great promises, the current performances lie far behind those of Li-ion batteries and many challenges remain to be tackled by the scientific community. My subject is part of this new adventure towards the development of solid-state batteries. The overall goal of this PhD is to identify performing cathode composite materials among the different systems available and to gain a deeper understanding on the parameters of paramount importance influencing their performances. Our work starts with a comparative survey of layered oxides-based solid-state batteries showing different stability, efficiency during the first cycle as well as different material utilization ratio. This screening enabled to point out carbon additive presence as favoring a higher active material utilization, but also as detrimental to both the cycle life of the battery and the first cycle efficiencies as it catalyzes decomposition reactions in thiophosphate-based SEs. We further embark ourselves in a study of Li6PS5Cl SE electrochemical stability in NMCs systems.Following this study on side reactions effects in solid-state sulfide-based system, we focused on the cathode composite transport phenomena evolution upon state of charge in Argyrodite-based systems. This switch was motivated by the necessity to understand another problematic aside from side reactions, namely the kinetic limitations hurdles observed in solid, preventing access to liquid cells performances.

**Mots-Clés:** All solid state batteries Impedance spectroscopy Ionic/Electronic conduction

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# Ln-MOF based ratiometric luminescent sensor for the detection of potential COVID-19 drugs

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Countless people have been affected by the COVID-19 pandemic on a global scale. Favipiravir, has shown potential as an effective drug for SARS-CoV-2, attracting scientists' attention. However, overuse of Favipiravir easily leads to serious side effects, requiring real-time monitoring in body fluids. Given this, a new lanthanide metal organic framework (MOF) was prepared under solvothermal conditions from either Eu (Eu-MOF or (1)) or Tb (Tb-MOF or (2)) using the highly delocalized imidazoledicarboxylic acid linker H2L (H2L = 5-(4-(imidazol-1-yl) phenyl) isophthalic acid) and could be successfully applied to selective optical detection of Favipiravir. In this MOF framework, the organic linker H2L provides a high excitation energy transfer efficiency that can sensitize luminescence in lanthanides. In addition, through deliberate tuning of Eu/Tb molar ratio and reaction concentration in the lanthanide framework, ratiometric recyclable luminescent **EuxTb1-x-MOF** nanoparticles with open metal sites have been constructed, which present a high detection sensitivity (Ksv = 1×107 (M-1), detection limit is 4.63 nM) for Favipiravir. The detection mechanism is discussed with the help of Density Functional Theory (DFT) calculations that sheds light over the selective sensing of Favipiravir over other related COVID-19 drug candidates. Finally, to explore the practical application of Favipiravir sensing, MOF based thin films have been used for visual detection of Favipiravir and recycled 5 times.

**Mots-Clés:** Ln, MOFratiometric luminescent sensorCOVID, 19 pandemicFavipiravir

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# Space charge doped 2D semiconductor diode

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The electrical contact with two-dimensional(2D) semiconductor materials is decisive to the electronic performance of the devices that depend on 2D semiconductors. To fabricate a vertical geometry junction between different concentrations of the same carriers, space charge doping is applied on a thick, intrinsically N-type semiconductor—Inse, to dope the surface to make a junction of N-type material and highly doped N-type material (NN+ junction). This vertical geometry junction is sensitive to the barrier height formed at the interface of semiconductor and metal, so the different metals used as electrodes have been investigated. In the framework of the possibilities of creating different barrier heights when different metals are in contact with InSe, I explored the possible explanation for the rectification in the previous samples. In addition, searching for the proper metal electrodes applied on semiconductors is active research at the moment, both experimentally and theoretically. This talk will introduce the device fabrication process and exploration of the rectification in the sample.

**Mots-Clés:** semiconductor, space charge doping

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# The Photothermal Effect of Nanoparticles for Optoelectronics

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Short-wave infrared (SWIR) typically refers to the photons in the wavelength range from 1 to 3 microns. It has many important applications such as gas sensing, medical diagnostics, night vision, etc. Developing new SWIR photodetectors with excellent performance is a top priority. in this thesis project, by employing new organic-inorganic hybrid device structures, we propose an alternative strategy for SWIR photodetection through harvesting the plasmonic-induced photothermal effect. In our design, The new SWIR photodetector, which is based on the combination of gold nanorods (Au NRs)/gold nanodisks (Au NDs) and VO2 thin films. Based on the photothermal properties of Au NRs/Au NDs, the nanogold structure will generate hot carriers on a time scale ranging from 1 to 100 fs, then the generating heat will be detected by a MIT (Metal-Insulator Transition) of VO2 thin films, then complete the photodetection process.

**Mots-Clés:** photodetector, photothermal effect, VO2

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