



RCP21 : Rencontres de Chimie-Physique 2021-SCF21

20-23 sept. 2021 Sète



Résumés





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Anne Zehnacker
Prix de la Chercheuse
Confirmée 2020



SPECTROSCOPY AND CHIRALITY

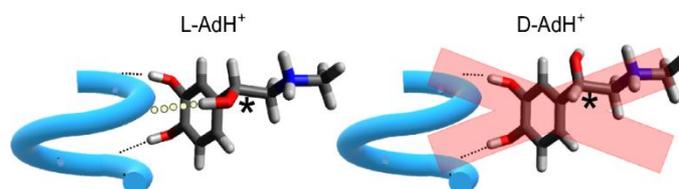
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Chirality plays an important role in shaping the molecular structure and the activity of biomolecules. Two enantiomers of a chiral molecule can be discriminated only when interrogated by a chiral probe. This probe can be of chemical nature (another chiral molecule) or of physical nature (a circular polarised light). Our group “Chirality and Spectroscopy” at ISMO uses the two approaches.¹ We are using and developing spectroscopic techniques for getting information on the role of stereochemistry in the structure and reactivity of chiral molecules.

In this talk, I will describe how laser spectroscopy in the gas phase sheds light on the forces responsible for chiral recognition at the molecular level, under supersonic jet conditions. On the example of small cyclic peptides, I will compare the results obtained in the gas phase to those obtained in the solid state by vibrational circular dichroism.²⁻³ I will then discuss molecular recognition of biomolecules under ion traps conditions, which give information on the interactions at play in neurotransmitters activity.⁴



Molecular interactions responsible for the recognition of L-Adrenalin (left) or D-Adrenalin (right) and its receptor (From Ref. 4)

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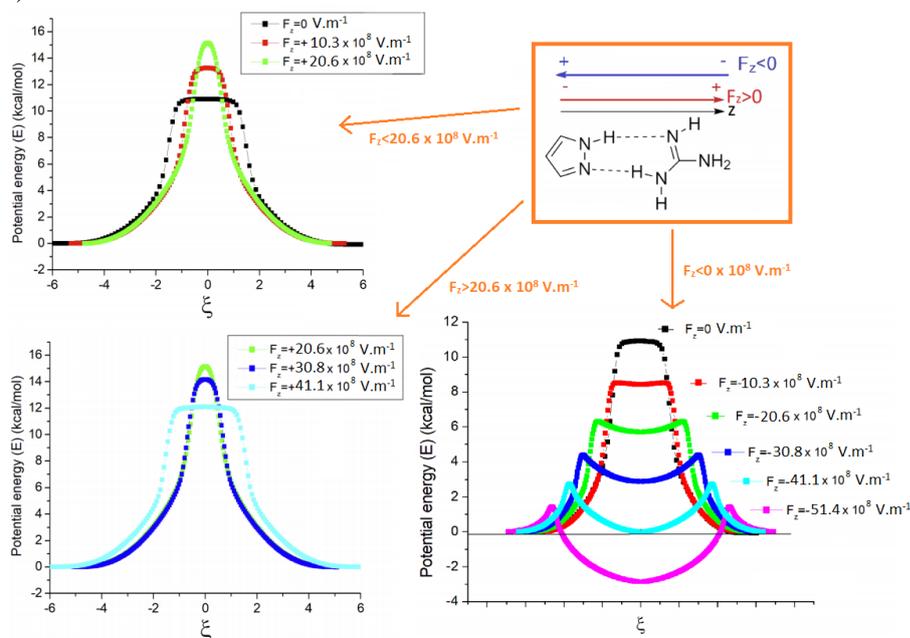
Influence of an oriented external electric field on double proton transfer reactions: from concerted to stepwise mechanism

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Double proton transfers (DPT) are important reactions in physics, chemistry and biochemistry. As an example, they are proposed to be responsible for some DNA mutations when they occur between Watson-Crick pairs [1]. Since at the heart of the double-helical DNA macromolecules or in the active site of enzymes, electric fields may reach $51.4 \times 10^8 \text{ V.m}^{-1}$, understanding the effect of an electric field on these reactions is fundamental. Matta *et al.* have already shown that it is possible to catalyze a DPT reaction using oriented external electric fields (OEEF) [2].

In this work, we studied the influence of an OEEF on the mechanism of DPT between Pyrazole and Guanidine by computational modelling, using DFT (ω B97XD/6-311++G(2d,2p)). This system was chosen as it is at the interface between a strongly asynchronous concerted mechanism and a stepwise reaction. Indeed, without OEEF, the potential energy profile along the reaction coordinate shows a wide plateau in the transition state region where the system has a strong zwitterionic character with deprotonated pyrazole in interaction with protonated guanidine [3]. We studied the reaction under the influence of an electric field oriented along the two proton transfers. In one direction, as the intensity of the field increases, we observed first an extinction of the plateau indicating that the two protons are transferred more synchronously, and then its reappearance, accompanied by an inversion in the order in which the two protons are transferred. In contrast, the concerted reaction is transformed into stepwise process under an electric field oriented in the negative direction. Finally, we explain the structural changes invoking the electronic reorganization along the reaction path within the topology of the electron localization function (ELF).



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Determination of Vibrational Circular Dichroism spectra of fluxional molecules through classical polarisable molecular dynamics

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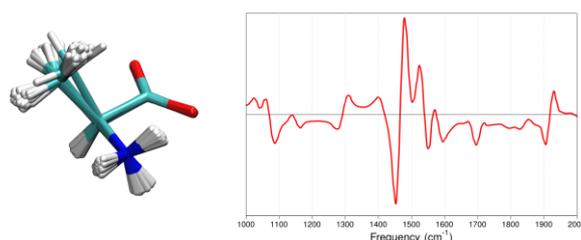
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Vibrational circular dichroism (VCD) is the weak difference in absorption for chiral molecules between right- and left- polarized light in the infrared range. It has promising applications in pharmacology owing to its ability to determine absolute configurations of chiral molecules. The shape of VCD spectra is highly sensitive to minor changes in conformation and molecular interactions, which makes it a sensitive probe of conformational isomerism and solvation [1].

In this work, several computational approaches were used to determine the VCD spectra of solvated fluxional molecules. The spectroscopic response of (1S,2S)-trans-1-amino-2-indanol in dimethyl sulfoxide (DMSO) was first investigated [2] by sampling its potential energy surface using the AMOEBA polarisable force field [6] through extensive molecular dynamics trajectories, the low-energy structures being then refined using density-functional theory for a limited number of solvent molecules. The VCD spectra computed for these microsolvated compounds allow the main effects of solvation to be captured, within the so-called cluster-in-a-liquid approach.

As an alternative to methods based on explicit descriptions of electronic structure [3,4,5] and to circumvent their limited sampling capabilities in time and space, we have also attempted to simulate the VCD spectrum directly from the molecular dynamics trajectories employing a polarisable force field, extending earlier efforts dedicated to the IR spectrum [7]. In this presentation, we describe our implementation of VCD spectroscopy in the Tinker software package [8] and our first applications to solvated amino acids, emphasizing the roles of temperature and the environment on the VCD spectrum.



Superimposed snapshots from a MD simulation of Alanine and its associated VCD spectrum

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Detection, structural elucidation and spectroscopic characterization of several tyrosine dimers

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Among major protein oxidative damages, di-tyrosine bridges have been evidenced in neurodegenerative or ageing-related diseases [1]. Combining oxidative radical production by gamma radiolysis with very performant chromatographic separation coupled to mass spectrometry detection, we brought into light new insights of tyrosine dimerization. No less than four different di-tyrosine bridges isomers have been highlighted while only two structures are characterized in the literature [2]. Through UPLC-MS analysis, specific Deuteration and isotopic (H/D) exchanges with the medium, we propose new original di-tyrosine types of crosslinking [3]. Absorption and fluorescence characterization of the four species were performed and consolidate our proposal. These results raise some questions about their respective role and toxicity *in vivo* as well as the legitimacy of using di-tyrosine as a biomarker.

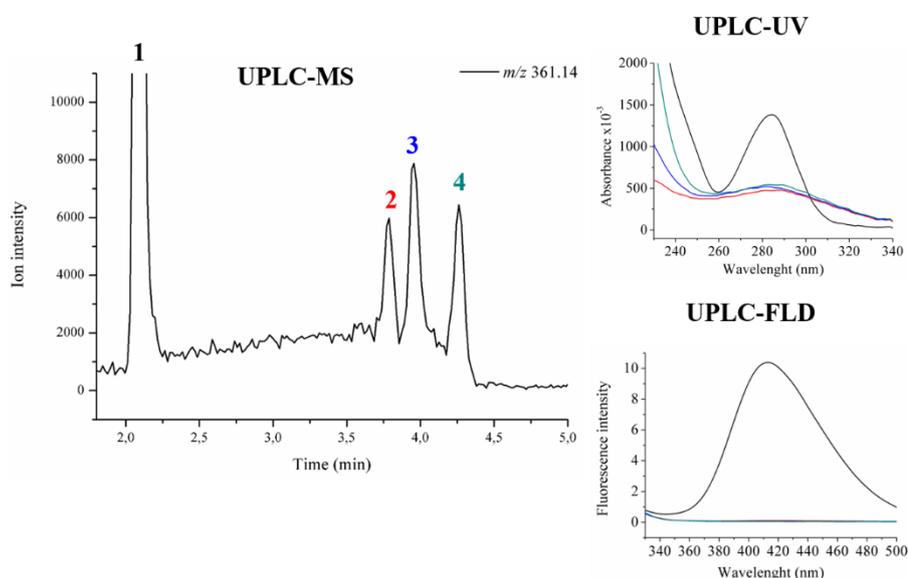


Figure 1: UPLC-MS, UPLC-UV and UPLC-FLD detection of di-tyrosine isomers

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FLUID ADSORPTION AND TRANSPORT IN NANOPOROUS MATERIALS

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Nanoporous materials are at the heart of numerous important applications: adsorption (gas sensing, drug delivery, chromatography), energy (hydrogen storage, fuel cells and batteries), environment (phase separation, water treatment, nuclear waste storage), Earth science (exchange between the soil and the atmosphere), etc. In this talk, we will present the state-of-the-art on adsorption/condensation and transport in nanoporous materials which possess pore sizes spanning several orders of magnitude (from the sub-nm scale to a few tens of nm) [1,2]. We will first discuss the different adsorption regimes encountered when a fluid is set in contact with a porous material: from irreversible adsorption/capillary condensation for the largest pores to reversible/continuous filling for the smallest pores. We will see that simple thermodynamic modeling allows rationalizing these different regimes provided that a description of the shift of the critical point of the confined fluid is taken into account. Then, we will show how transport in such media can be described without having to rely on macroscopic concepts such as hydrodynamics [3,4,5]. Using parameters and coefficients available to experiments, we will see how transport coefficients can be rigorously obtained from simple models in the framework of Statistical Mechanics using models such as free volume theory and intermittent brownian motion [6].

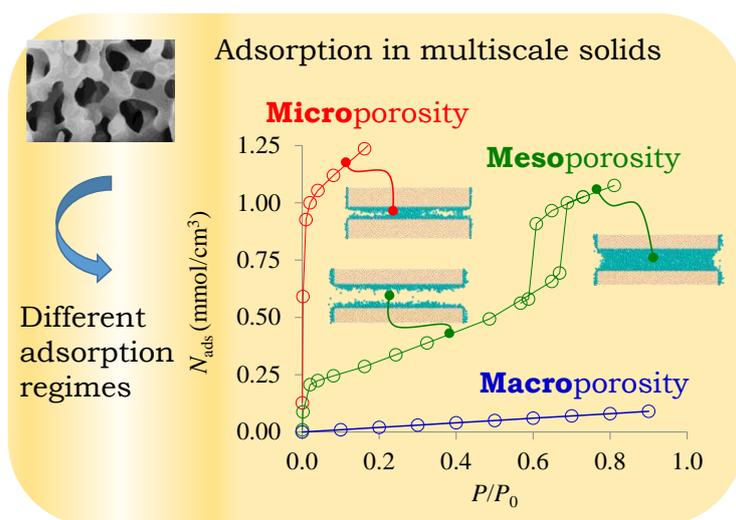


Fig. 1. Adsorption in cylindrical silica pores of different sizes. Most real porous materials exhibit a broad pore size distribution with pore voids ranging from the nm scale to the macroscopic scale. These different pore sizes will be considered as well as the case of hierarchical porous solids combining all these different scales.

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Multifunctional surface patterning of chalcogenide glasses by thermal poling.

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Chalcogenide (ChG) glasses, due to their wide transparency domain spanning from near infrared (IR) to mid-IR, constitute highly attractive optical materials for sensing applications. In addition, their properties can be easily tuned by slight modifications of their compositions. In the context of integrated photonics, there is an increasing need for materials in which different functionalities are controlled at the micrometer scale such as linear and nonlinear optical response, electrical and/or chemical properties. In the present work, we demonstrate the control of two surface properties (electrical surface potential and chemical reactivity) by a single process: a thermo-electrical imprinting process or micro-poling. The latter consists in applying a strong DC voltage to a glassy material heated at moderated temperature (under its glass transition temperature) and bringing it back to ambient temperature before removal of the electric constrain. It is referred to as an “imprinting process” in the sense that the anode applying the DC voltage is constituted of a conductive pattern that is transferred to the glass surface after the process.

Different series of glasses in the Ge-Sb-S-Na system were developed with varying S to Ge content and varying sodium concentration in order to establish the respective influence of these two parameters. A first study based on Raman microscopy has revealed similar structural evolutions whether sodium was removed from the composition or whether it was removed via poling. This demonstrates the flexibility of the glass matrix that can rearrange itself under a strong electrical constraint.

On the basis of this methodology regarding the choices of compositions – individual influence of the sodium and of the Sulphur contents – we found optimal parameters that lead to the control of our two functions, namely the surface electrical potential and the surface reactivity. Firstly, AFM measurements in Kelvin Probe mode (KPFM) have shown that, close to the Sulphur stoichiometry and at low sodium content, micro-poling resulted in a micrometer scale patterning of the surface electrical potential, varying in sign and with up to a 9 V amplitude range.^[1] This response decreases with time, yet it is stable enough to be detected even after two years. These promising results allow considering these surfaces for new multifunctional devices such as chemical and/or biological detectors. Secondly, at higher sodium and Sulphur contents, micro-poling resulted in considerable difference between the reactivity of poled and of the non-poled zones. This difference offers the possibility to selectively etch the surface of these glasses. Thereby, through a rather simple process (micro-poling followed by a dissolution in an amine solvent for less than a minute), it is possible to control at the micrometre scale, the topology of these glasses on large (centimetre scale) surfaces. This approach could be a way to generate photonic features (waveguides, metasurfaces...) at low cost and could be an alternative to classical lithography techniques.

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Extreme environments host bacteria adapted to withstand conditions that are a priori harmful to any living organism. The metalloenzymes which catalyze within these microorganisms numerous chemical reactions necessary for their metabolism, exhibit themselves outstanding properties. They thus appear as attractive catalysts for developing sustainable biotechnologies. Resistance to high salt concentrations, high temperatures, presence of metals, activity in conditions of low pH and substrate concentration ... these are the factors whose impact on the electrocatalysis of the reduction of oxygen and the oxidation of hydrogen have been studied. Thanks to the knowledge of the molecular basis which ensure an optimal electron transfer to electrodes, the interest of the use of these extremozymes in a high temperature enzymatic fuel cell is demonstrated.

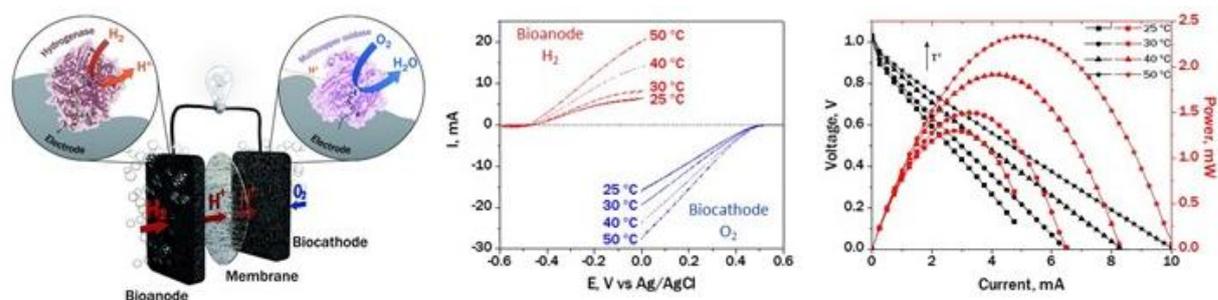


Fig. 1 Performance of the enzymatic fuel cell based on the hyperthermophilic hydrogenase from *A. aeolicus* and on the thermostable bilirubin oxidase from *B. pumilus*.

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An electrochemical aptamer-based biosensor for arginin-vasopressin

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Antidiuretic hormone (ADH), also called arginin-vasopressin (AVP), is an hypothalamus synthesized hormone which is released from the posterior pituitary in response to plasmatic hyperosmolarity; it promotes water reabsorption from the distal renal tube. Vasopressin is of particular clinical interest in the diagnosis of diabetes insipidus in the follow-up of patients with heart failure, hyponatremia or polyuria.

To meet the need for quantification of AVP in plasma, radioimmunoassays (RIA) approaches have been early developed^{[1][2]} and are still currently used as reference method^[3]. Much more sensitive methods such as liquid chromatography (LC) mass spectrometry (MS) are now emerging^{[4][5]}. However, although very sensitive (up to 0,2 pmol/L of limit of quantification for LC-MS^[5]), these methods are generally complex and may require relatively large equipment.

For several years, the NOVA team of the DPM has been working on the development of new detection methods using aptamers which have gained widespread attention as biorecognition elements, especially for small molecules^[6]. They have used aptamers with optical signal transduction for several small targets and very recently for the AVP^[7] assay. But unfortunately, the detection limit obtained (around 10 nM) by fluorescence polarization method was not sufficient to quantify the hormone in human serum (picomolar quantity).

The aim of our work is to develop a new detection method of AVP using an aptamer as biorecognition element with sensitive electrochemical transduction the detection limits of which are close to the femtomolar level^[8]. In addition, electrochemical biosensors can be miniaturized into portable analytical devices with a possibility of wireless transmission of the result.

The first step of our work is the modification of the aptamer by the biotin function which will allow its immobilization on the surface of the electrode, itself modified by a thin film of polypyrrole-NTA (nitrilotriacetic acid). The immobilization of the AVP aptamer is performed by coordination with Cu²⁺ complexed in NTA^[9]. The recognition of vasopressin by the aptamer induces a quantifiable electrochemical signal which is correlated with the amount of vasopressin bound to the surface of the pre-modified electrode (Figure 1).

A well-developed protocol for the new designed aptasensor will allow the application of the system on clinical samples as the final part of our work.

At the moment, we are working with the DNA serial AVP aptamer using Electrochemical Impedance Spectroscopy (EIS) as signal characterization technique. The initial results are encouraging and further studies should help finding out the best conditions for the system to reach a good sensitivity.

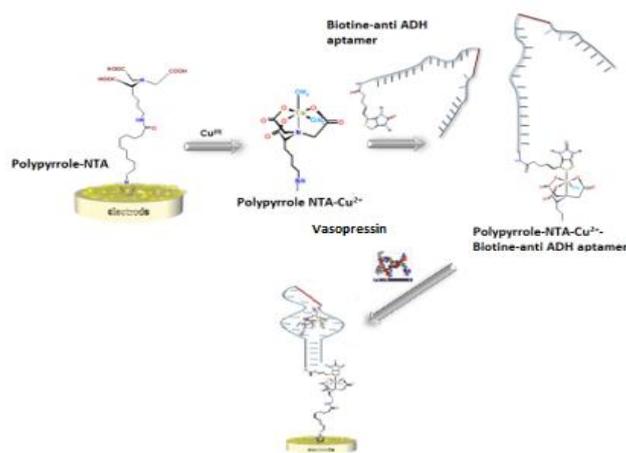


Figure 1: Schematic of the construction of the electrochemical aptasensor

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Functionalized electrochemical sensor for the detection of metallic trace elements in water

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It is nowadays well known that metallic trace elements (MTEs) are an issue for public health despite their low concentration and are responsible from harmful diseases. Thus, it is necessary to detect and to quantify them for public wellness. The usual way to control their presence in water consists of taking samples and of sending them for analysis on heavy and expensive instruments as ICP-MS. However, less expensive and portable analytical systems, allowing the analysis on-site, would contribute to improve water monitoring. Electrochemical sensors are promising since they are easy-to-use and low-cost portable systems, allowing a selective analysis of MTEs, bringing real advantages to food or environmental controls [1-2].

For this purpose, we design, manufacture and functionalize by specific ligands carbon-based electrodes (glassy carbon, Pyrolyzed Photoresist Films) to assure a good selectivity to the targeted metal. The functionalization of the electrode was performed by electroreduction of aryldiazonium salts leading to COOH groups on its surface [3]. The ligand was then immobilized by a chemical coupling reaction. The modified surfaces were analyzed by XPS. The analytical method composed by a preconcentration step at open circuit followed by anodic stripping voltammetry was optimized to detect cadmium ions at low concentrations around 10^{-8} M.

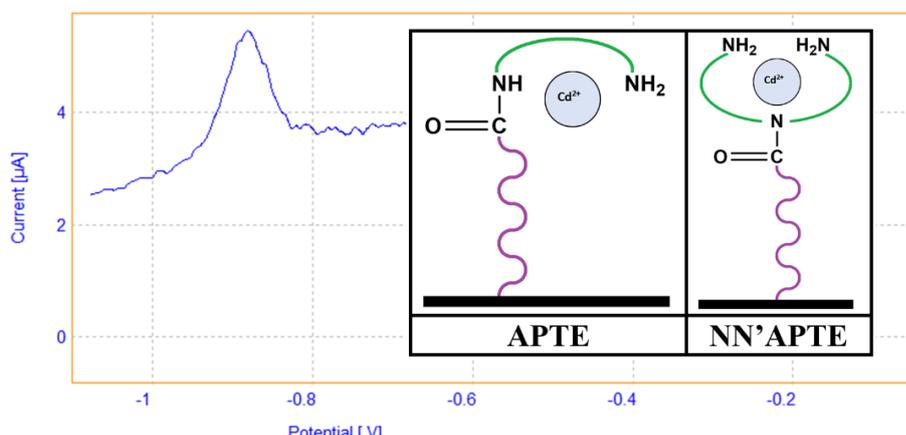


Figure 1 : Electrochemical signal of Cadmium at $2 \cdot 10^{-7}$ M detected by its specific ligands APTE and NN'APTE

After optimization of all parameters, sensor performance was investigated in terms of detection and quantification limits, reproducibility and specificity towards interfering metals. The effect of the electrografting method leading to mono or multilayers on the performance of the sensor was considered. This EASCV-sens project was funded by the French national agency (ANR-18-CE42-0011, Programme AAPG 2018).

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20-23 sept. 2021 Sète



Rémi Dupuy

Prix de Thèse 2020



Société Chimique de France



Société Française
de Physique

Direct and indirect photon-induced desorption from water ice

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Water ice is ubiquitous on Earth and in space and plays an important role across many different scientific fields. It is, for instance, the main component of the ice mantle of molecules covering interstellar dust grains. In the interstellar medium, processes such as photon-induced desorption play a key role in the exchanges between this icy solid phase and the gas phase. A better understanding of such processes is thereby required to model astronomical observations of molecules in space and gain a deeper understanding of the complex and exotic chemistry of star and planet-forming regions.

Photon-induced desorption from pure water ice has been the object of several experimental and theoretical investigation in the past. Different photodesorption mechanisms have been proposed but so far no agreement has been found on the dominance of any single mechanism. Here I will present new results on the isotopic and temperature dependence of photodesorption from pure water ice and discuss the implications in terms of desorption mechanism. More complex systems containing other molecules in addition to water have also been little explored. I will also present results on the indirect desorption [1], i.e. desorption induced by excitation of the water ice matrix, of other small species adsorbed at the surface of water ice. In this case we are able to clearly identify the desorption mechanism.

[1] *Mechanism of Indirect Photon-Induced Desorption at the Water Ice Surface*

R. Dupuy, M. Bertin, G. Féraud, X. Michaut, P. Marie-Jeanne, P. Jeseck, L. Philippe, V. Baglin, R. Cimino, C. Romanzin, and J.-H. Fillion. **Phys. Rev. Lett.** 126, 156001 (2021)

Development of a novel cationic exchange membrane based on graphene oxide for application in a microbial fuel cell

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The role of membranes in a dual-chamber microbial fuel cell (MFC) is not only to provide the separation of both compartments but also to facilitate the proton transfer from the anode to the cathode chamber¹. Recent studies have focused on developing membranes with polymeric structure to replace the commercial membrane of Nafion[®] due to its some limitations. In the present study our team aimed at developing a cationic exchange membrane that favor the selective transport of protons due to the presence of graphene oxide and its functionalized form. Generally, there are negatively charged groups, such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$ or $-\text{PO}_3\text{H}^-$, fixed to the membrane backbone of CEMs, enabling them for a selective permeability to the cations.

To do so, we have selected the polyethersulfone (PES) as the polymeric structure and then sulfonated it (SPES) using the concentrated sulfuric acid (H_2SO_4) to make it conductive. The next step was to synthesize the graphene oxide (GO) using the Hummer's method² and functionalized it by adding $-\text{SH}$ groups through the thiolation process in a reflux by phosphorus pentasulfide (P_4S_{10})³. Finally, the cation exchange membranes (CEMs) were prepared using the membrane solution casting followed by solvent evaporation technique. Herein, we named the final membrane as SPES/TGO which defines the structure of sulfonated polyethersulfone/thiolated graphene oxide. The synthesized membranes were characterized by ATR-FTIR spectroscopy, and FEG-SEM. Also, the water uptake, transference number (H^+ , Li^+ , Na^+ and K^+), contact angle and zetâ potential of newly developed membranes were evaluated. These analyses provide us with the opportunity of studying the role of presence of thiolated groups in a membrane structure comparing to the bare SPES membranes. We followed the performance of membranes in a dual-chamber MFC to study their efficiency for proton transfer and meeting the needs of this environmentally-friendly technology.

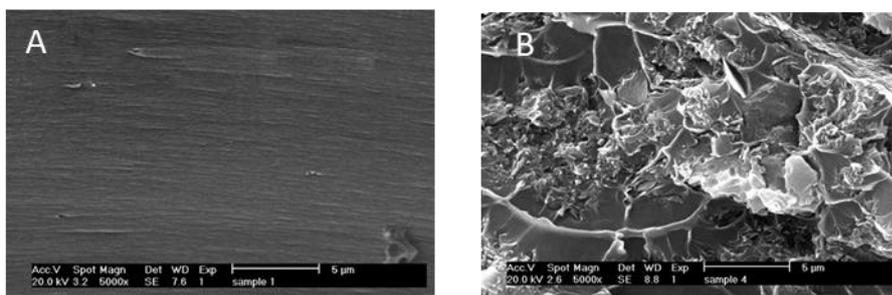


Fig 1- SEM cross section of A) SPES and B) SPES/TGO membranes

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Clathrate hydrates FTIR spectroscopy: a key in understanding solar system ices

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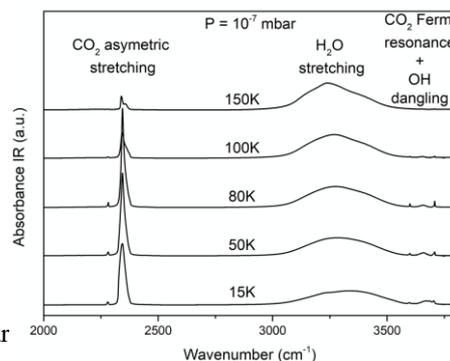
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Hydrates are ice-like crystalline compounds, resulting from the tridimensional stacking of cages of H-bonded water molecules. Clathrates are gas hydrates, meaning that the guests are gas molecules encased in a host framework of water molecules. The formation of clathrate hydrates may play a key role in the stability of volatile species in many astrophysical bodies, such as comets. They may provide a trapping mechanism responsible for the preservation in the solid state of volatile species at temperatures higher than expected for the pure solid, thus avoiding their early escape. Observations of comets suggest that there is a mechanism still unknown which could explain part of the phenomena linked to cometary activity, in relation to the survival of these volatile molecules [1].

Gas hydrates only form and remain stable in specific temperature and pressure regimes that depend on the nature of the guest molecules [2]. Theoretical phase diagram of clathrate hydrates show that it would be possible to form clathrates at very low pressure (10^{-10} bar) and temperature (< 80 K), but there is a lack of experimental data using these preparation methods [3]. Could clathrate hydrates be formed under such conditions? What if the formation and characterization of these ice-like structures under such conditions could provide valuable experimental evidence for understanding the origin and evolution of comets?

FTIR spectroscopic identification of carbon dioxide and methane hydrates have been performed at low temperature (10 K) and pressure (base pressure 10^{-7} mbar) regimes. In an effort to understand the nature of the gas hydrates formed under these conditions, vibrational spectra of distinct gas/ice interactions (clathrate hydrate, gas in/on water ice) were compared. The behaviour of the water crystalline skeleton interactions with the trapped molecules at different temperatures, as well as the influence of the gas mixture and the deposition method, will be presented.



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Experimental study of X-ray photon-induced desorption from methanol-containing ices and its astrophysical implications

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Methanol CH₃OH is a small organic molecule of particular importance in astrophysics. It has recently been detected in its gaseous form in protoplanetary disks ([1], [2]) and its formation is supposed to be the first step toward a complex organic chemistry. Its presence in these star-forming regions is still not fully understood. It is generally believed to form on the surface of cold ($T < 100$ K) dust grains, in condensed phase, diluted in the main constituents of the icy mantles, H₂O and/or CO. As it cannot thermally desorb from these ices, a non-thermal process should explain its gas phase presence. In protoplanetary disks, it is expected that X-rays emitted by the central young stellar object could trigger CH₃OH ejection from the ices into the gas phase, hence explaining the detections. This process, known as X-ray photodesorption, can participate to the overall gas-to-ice ratio of methanol in these cold regions and needs to be quantify.

Experimental study of X-ray photodesorption from methanol-containing ices has been achieved in the range of 500-570 eV by coupling the Ultrahigh Vacuum SPICES setup to the SEXTANTS beamline of the SOLEIL synchrotron facility in Paris-Saclay. The diversity and richness of the desorbing molecules from the studied ices is probed by mass spectrometry. This allows to derive quantitative X-ray photodesorption yields that are representative of the efficiency of X-rays to desorb a given molecule. The critical influence of several parameters on these yields, such as the ice composition (mainly the influence of CO and H₂O molecules) and the incident photon energy, allows to shed light on the chemical and physical mechanisms at play in these X-ray irradiated organic ices. In this context, I will present the main findings of these experiments and I will discuss their astrophysical implications.

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RCP21 : Rencontres de Chimie-Physique 2021-SCF21

20-23 sept. 2021 Sète



David Talaga et Sébastien
Bonhommeau
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TOTAL INTERNAL REFLECTION DARK-FIELD SCATTERING AND ENHANCED RAMAN SCATTERING MICROSCOPIES COUPLED TO ATOMIC FORCE MICROSCOPY

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An instrument allowing for colocalized imaging by atomic force microscopy (AFM), dark-field scattering (DFS) and surface-enhanced Raman scattering (SERS) microscopies of noble metal nanoparticles is presented (**Fig. 1**). A high numerical aperture total internal reflection (TIR) objective is used to probe the polarization dependence of DFS spectra associated with single nanoparticles, which reveals the degree of anisotropy and can be correlated to the morphology and the orientation observed on AFM images.^[1] Under convenient continuous laser excitation, intense SERS signatures can then be detected.^[1,2] This technique can also be applied to the study of optical nanosources relevant in tip-enhanced Raman spectroscopy (TERS), to determine the ideal laser excitation to perform nanoscale chemical imaging.^[3] With the very same instrument, a TIR Raman spectroscopic method is also presented. Through the investigation of two examples,^[4,5] the high anisotropy of the electric field in evanescent regime is exploited to optimize the detection of Raman signals in SERS and TERS.



Fig. 1 AFM/DFS/Raman instrument with a magnification of the accessory for TIR light injection.

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Probing isomerization dynamics and thermodynamics using tandem ion mobility spectrometry

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We report an original approach, based on tandem ion mobility spectrometry (IMS) [1] to monitor the dynamics of structural changes in isolated molecular ions.[2] The first IMS stage allows selecting one isomer of the ions under study. Selected species are then stored for a controlled amount of time in a thermalized ion trap. The second IMS stage, is used to probe the final state of the ions, which are finally detected by a mass spectrometer. Changes in both the ions conformation/configuration and mass is then possible to detect as a function of trapping time. Such temperature-dependent isomerization kinetics measurements provide direct information on the associated thermodynamic quantities.

We will show an application of this simple procedure to map the local conformational landscape of Glu-Fibrinopeptide-B, which was found to display structural bistability in the gas phase. We also show that the measured thermodynamics quantities are directly comparable to observables from ensemble molecular mechanics simulations.[3]

As a second example, we investigated the back-isomerization dynamics of the photoisomer of an azobenzene derivative. An interest of our approach is that it allows probing temperature ranges significantly higher than those attainable in solution, which in turn drastically shortens the time required for the kinetics measurements. This is particularly interesting for the present species whose high back-isomerization barrier yields lifetimes of several days at room temperature (see Figure).

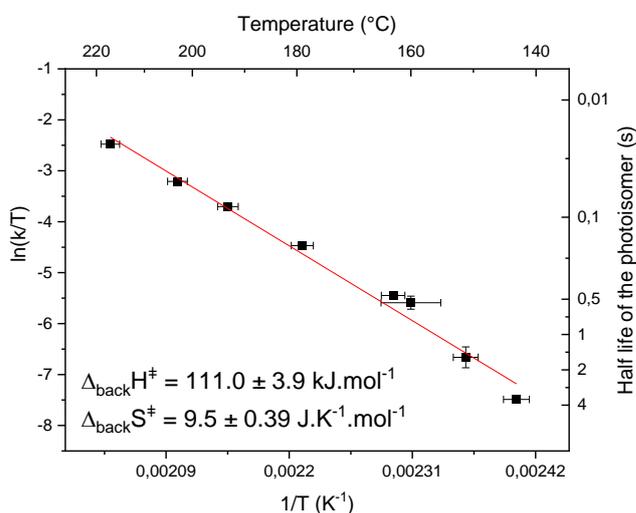


Figure 1: Eyring's plot obtained after tandem IMS measurements of the isomerization kinetics of an azobenzene derivative. The derived values for the entropy and enthalpy of the transition state are provided.

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Evaporation process of SOA-like droplets highlighted by an innovative experimental set up

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Atmospheric aerosols are well known to impact both air quality and climate change. In the atmosphere, secondary organic aerosols (SOAs) are formed through the gas-phase oxidation of both anthropogenic and biogenic volatile organic compounds (BVOCs), such as toluene, α -pinene, etc., by atmospheric oxidants (ozone, OH and NO₃ radicals). Once generated, they may further react through aging multiphasic processes. These reactions may affect both the chemical composition and the physical properties of aerosols such as surface tension, hygroscopicity, viscosity and gas-particle partitioning. In the laboratory, the particle aging is usually investigated using two experimental approaches: (i) atmospheric simulation chambers and (ii) flow reactors. However, the complexity of aerosol aging processes occurring at the gas/particle interface is still not well described. Recent developments using single particle approaches allow studying various chemical aging processes and microphysical properties at the particle scale^[1-4]. In this context, the objective of the present work was to characterize the gas-phase partitioning of individual SOA-like particles. The evaporation behavior of aqueous-diluted linalool single droplet was investigated under high relative humidity (RH) using an innovative experimental set-up coupling an acoustic levitation cell with a Raman microspectrometer (RMS) and a proton-transfer-reaction mass spectrometer (PTR-MS). Thus, both gaseous phase and particle composition were probed during the evaporation process with *in situ* and on line conditions.

The influence of initial linalool concentration (up to the solubility limit), initial droplet size and RH variation (80-98 %) has been investigated by following the particle size (d^2/d_0^2) and the gaseous and particulate compositions. Experimental results were successfully compared to the theoretical “ d^2 law” approach^[4-5]. New highlights in SOA-like particle behavior at high relative humidity will be presented at the individual particle scale.

Acknowledgements

Authors thank the University of Bordeaux, ADEME and CNRS-INSU LEFE-CHAT program, for financial support.

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Investigation of the adsorption of CH₃I on NaCl and ice surfaces

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Iodine-131 can be released during a severe nuclear accident and can be carcinogenic for humans [1]. In the literature, there are missing pieces of knowledge about inter-actions between iodinated compounds and aerosols in the troposphere. In this context, this work consists in investigating the adsorption on sea salt aerosols and ice of gaseous iodomethane (CH₃I). A force field has been parametrized and used in classical molecular dynamics calculations. This method allows to sample large systems and a wide range of configurations. These configurations serve as starting geometries in a QM/QM' ONIOM [2, 3] approach to compute the IR frequencies. In addition, periodic ab initio calculations have been carried out [4, 5]. Adsorption energies and vibrational frequency shifts upon adsorption are thus quantified. We show that the vibrational frequency shifts are small, mainly because there is no strong coupling between the adsorbates and the surfaces. We also illustrate the differences on the adsorption between the crystal and amorphous ice at low temperature.

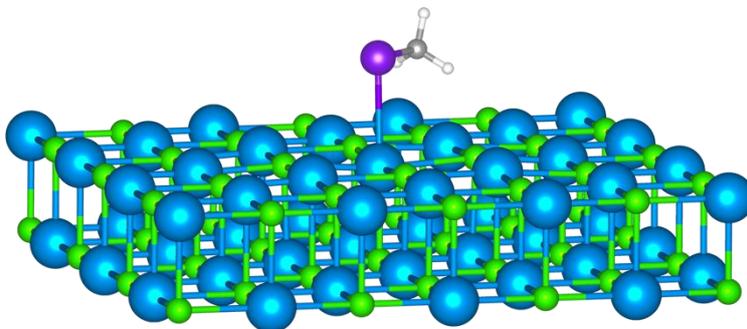


Figure: Optimized geometry of CH₃I adsorbed on a dry NaCl(100) surface from a QM/QM' ONIOM (DFT/PM7) calculation.

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Acknowledgements:

- PIA MiRE (ANR-11-LABX-0005-01)
- I-SITE ULNE OVERSEE project (contract ANR-16-IDEX-004)

Catalytic conversion of CO₂ into α -alkylidene cyclic carbonates: a comprehensive mechanistic study

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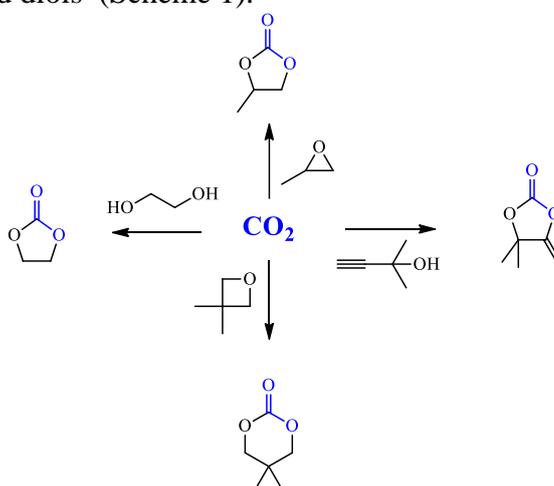
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The use of carbon dioxide both as a substitute to harmful and/or volatile organic solvents and as a cheap and ecofriendly C1 chemical reactant has been the subject of a particular attention in the last years.^[1] Many reactions involving CO₂ utilization as a raw material have been described, especially for the synthesis of cyclic carbonates via the coupling of CO₂ with different substrates such as epoxides, oxetanes, propargylic alcohols and diols (Scheme 1).

In particular, the catalytic synthesis of α -alkylidene cyclic carbonates (CCs) by the carboxylative coupling of CO₂ with propargylic alcohols has gained interest recently. α CCs differ in their structure from conventional CCs by the presence of an exocyclic olefinic group that facilitates the ring-opening of the cyclic carbonate by various nucleophiles such as amines and alcohols. However, efforts are still needed to identify more stable, cheaper, and less/nontoxic organic catalysts that promote the selective carboxylative coupling of CO₂ with propargylic alcohols under mild conditions. In this context, this communication report about the use of a series of organic salts as catalysts for the coupling of CO₂



Scheme 1: Conversion of CO₂ into cyclic carbonates

with 2-methyl-3-butyn-2-ol to form α -methylene cyclic carbonates. We investigated the influence of the modulation of the structure of the organocatalyst on the catalytic performances. The optimum activity resulted from the best compromise between the ion pair separation controlled by steric effects and the basicity of the anion. Kinetic investigations by in situ Attenuated Total Reflectance (ATR)-Infrared (IR) spectroscopy correlated to DFT calculations were performed on the most active and selective catalysts. The unusual kinetic profiles were related to a remarkable evolution of the hydrogen bonding solvation of the catalyst during the reaction.^[2] Finally, using a co-catalyst, we were able to strongly improve the reaction kinetics under milder condition while keeping a good selectivity that allowed us to propose a domino approach for the synthesis of oxo-alkyl carbonate scaffolds and polycarbonates from CO₂, propargylic alcohols, and monoalcohols under mild operating conditions (pCO₂ = 1–15 bar, T = 40–80 °C).^[3]

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GRAVIMETRIC TOOLS: OPERATION, POSSIBILITIES AND APPLICATIONS.

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Gravimetric sensors are inexpensive devices which, in a first approach, allow the measurement of mass variations in the range of ten nanograms performed in air or in contact with a liquid. In general, they are referred to quartz crystal microbalances (QCM) and operate according to chronometric principles based on piezoelectric quartz resonators. An oscillator is used to recover the resonance frequency, which is itself related to variations in mass of a certain film deposited on the QCM: a linear relationship, known as Sauerbrey equation, is established between these variations in frequency and mass. However, different conditions must be respected in order to use this equation because the devices are sensitive to other quantities such as the roughness/mechanics of the films studied, and the characteristics of the electrolyte in contact with these films. In terms of gravimetric sensitivities, typically it is possible to measure mass variations of a few nanograms for resonance frequencies of around a few MHz.

Different applications are possible with these gravimetric sensors and the main domains which can be explored are in health [1,2], environment [3,4] or energy [5,6] from both a fundamental and an applied point of view.

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Electronic absorption energy and structure relationship in polycyclic aromatic hydrocarbon dimers

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The formation of soot is a complex process that is still not fully understood despite its primary importance for environmental and health matters. A consensus was reached on the fact that polycyclic aromatic hydrocarbons (PAHs) play a major role in the process, however, the transitioning from gaseous molecules to solid black particles remains a mystery. [1] In flames, it is observed that the excitation energy required to obtain a fluorescence signal in the soot nucleation zone is red-shifted compared to that obtained from the PAH zone. [2] In our work, we explored the possibility of PAH collisions in flames leading to the formation of a dimer as the first step before the clustering. In particular, using DFT and TD-DFT we investigated the effect of the dimerization on the structural and spectral properties of a range of medium-sized PAHs such as pyrene, fluoranthene or perylene. The selected geometries consisted of purely physical dimers bonded by van der Waals forces, and hybrid chemical – physical systems, bonded by a covalent bridge. We calculated the electronic transition energies of all dimers and studied the correlation of the energy shift upon dimerization to structural parameters in order to help interpreting the experimental data.

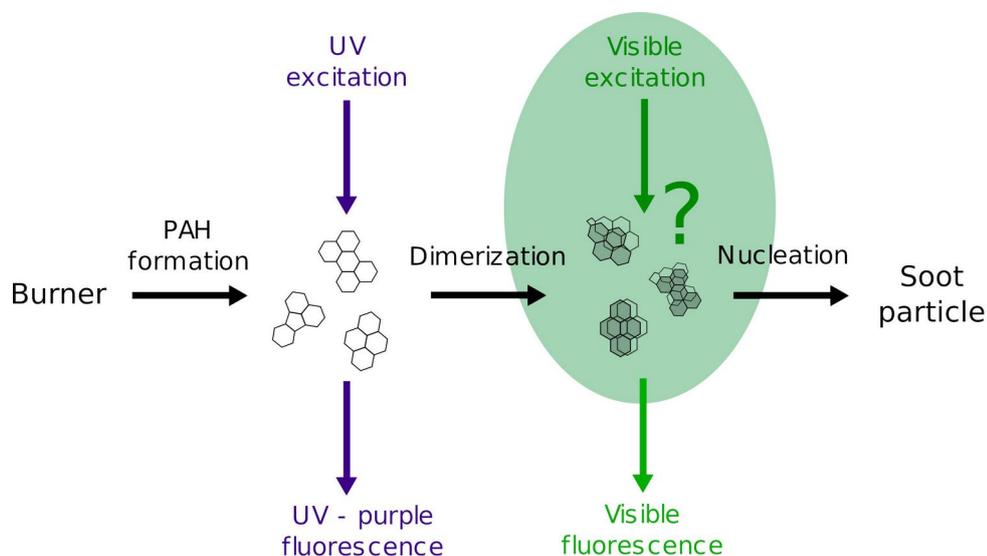


Figure: Representation of the soot formation process in flames. The green area represents the topic of our computational study

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Usage of plant viruses as a biocompatible scaffold for the development of magnetic nano biohybrids for biomedical applications.

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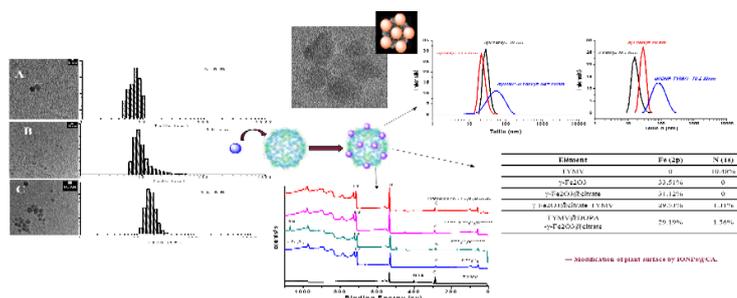
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In the last few years the developments of new bionanomaterials using magnetic nanoparticles and the three-dimensional (3D) plants structures as platforms have opened many new opportunities in biomedical applications, such as for targeting, therapeutic delivery, MRI contrast enhancement, and hyperthermia. [1]

The first part of my work focus on the synthesis, functionalization and characterization of iron oxide nanoparticles (IONP). We synthesized IONP using the polyol method with different size and functionalized with citric acid as a coating molecule to stabilize their suspension in water. These nanoparticles were characterized by DLS, SEM and TEM showed diameters of 5, 10 and 15 nm. DRX, XPS and FTIR experiments were performed to ensure the success of the coating process. The ZFC/FC magnetization, magnetic hysteresis and SQUID measurements revealed superparamagnetism of nanoparticles and high saturation magnetization 60, 70 and 73 emu /g for the 5, 10, and 15 nm respectively. In order to enhance their magnetic properties, the second part focus on grafting by peptide bonds these IONP on icosahedral and rod-shaped viruses using Turnip yellow mosaic virus (TYMV), Rice yellow mottle virus (RYMV) and Tobacco mosaic virus (TMV) due to their peculiar properties: easy accessibility made, rigidity, highly functional surface, structural symmetry and nanoscale dimensions [2-3]. After purification, the resulting bionanomaterials were characterized by light scattering (DLS) confirmed the grafting through the hydrodynamic size increase by comparing IONP and capsid alone to γ -Fe₂O₃-viruses and Transmission electronic microscopy (TEM) observations revealed that IONP were well organized with 5-fold symmetry around the capsid.

For further studies, we shall improve the yield of this reaction, and we will measure the magnetic properties of these new bionanomaterials and compare them to those of ungrafted IONP.



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Theoretical study and design of a new class of photoswitches based on the Excited-State Cation Transfer

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We propose to study a new class of photoswitch and the corresponding elementary photoinduced reaction, the so-called Excited-State Cation Transfer (ESCT). This reaction relies on photo-release/photo-complexation of cations: after irradiation, the cation is translocated from a complexation site 1 to a site 2 during the excited state lifetime. Our purpose is to develop an innovative approach, relying on organic synthesis, spectroscopy and theoretical chemistry, to trigger photoswitching properties through the control of the ion position in molecular bi-chelator systems. So far, some examples in the literature dealt with either photo-release or complexation of cations and a decisive breakthrough would consist in combining those two processes via the design and synthesis of ESCT photoswitches.

Inspired by the work of Moore and coworkers on photoejection and recapture of cations on organometallic complexes, we were able to set up descriptors based on the analysis of excited state properties as well as on photoinduced charge transfer properties⁽¹⁻⁵⁾. These descriptors were then applied to a family of organic molecules, the pyridinium betaines for which an ejection of the cation from the imidazole bridge (site 1) takes place, without recapture of the cation by an azacrown (site 2)⁽⁶⁾.

Therefore, we improve the photoswitching process by a methodical design strategy based on the phenomenon of photoejection of the cation from site 1, the increase of the ground state complexation constant of sites 1 and 2 (K_1 and K_2 , respectively) as well as the decrease of the excited state complexation constant of site 1, $\log K_1^*$, in order for the parameter $K_1 > K_2 > K_1^*$ to be always satisfied.

We present here the impact of the modification of the complexation sites on these complexation constants as well as on its optical properties to allow the constitution of an efficient ESCT photoswitch.

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Conférence Jean Perrin



The Alchemy of Vacuum - Hybridizing Light and Matter -

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Light-matter interactions are not only fundamental for the existence of life, such as we know it, but play a key role in our culture and our technology. What is perhaps more surprising, is that light-matter interactions occur even in total darkness. This is because vacuum, the three-dimensional space in which we exist, is not a void but is full of quantum fluctuations, including electromagnetic fluctuations which affect for instance the forces between molecules. When such light-interactions become strong enough, a new regime arises characterized by the formation of hybrid light-matter states. This is the so-called strong coupling regime which leads to fundamental changes in material properties. After introducing some of the basic concepts, examples of modified material properties such as chemical reactivity and energy transfer will be presented.

Sugar peptide interactions in the gas phase: structure, conformation and the role of water.

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Sugars are complex flexible biomolecules that can adopt multiple conformations influenced by the interactions with surrounding molecular partners such as solvent molecules or other biomolecules. The bioactive forms of such assemblies are governed by the combination of intrinsic properties of each molecular components as well as by their intermolecular arrangement. Monitoring the *intermolecular* interactions at play and their balance with *intramolecular* preferences provides key information on affinity and selectivity.

Gas phase conformer selective and vibrationally resolved spectroscopic methods, complemented by computational conformational landscapes exploration, uniquely probe local molecular interactions. In the near infrared, between 3.5 and 4 μm , we can probe intramolecular stretching modes of O-H and N-H groups, which are directly involved in the intra- and intermolecular interactions as donors and acceptors and determine the structure and conformation of complex molecular assemblies made of significant models.

We have applied this approach to study the structural and conformational properties of non-covalent complexes composed of a monosaccharide, models of peptides and water molecules. These represent ideal size controlled systems to interrogate the structural basis of sugar-protein interaction and water. Our recent observation of ternary sugar-peptide-water complexes opens new opportunities to question the role of water in molecular recognition processes on the structural point of view.

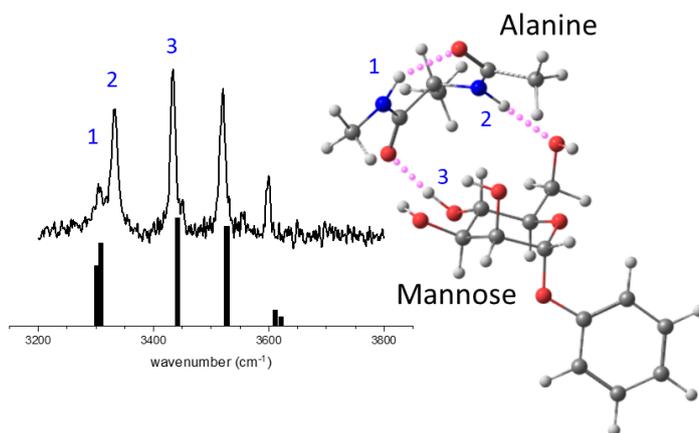


Figure 1: Experimental and computed vibrational spectra of the (Ac-Ala-NHMe)-(Mannose) complex.

From darkness to light: fluorescence photoswitching using negative photochromic imidazole dimer

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Negative photochromic compounds are molecules that are colored in their stable form and become colorless under visible irradiation. When they are combined with a fluorophore, an “OFF-ON” fluorescence modulation can be achieved, through an energy transfer process [1]. This type of modulation allows to obtain a better contrast than conventional “ON-OFF” fluorescence photoswitching due to the initial dark state. Moreover, a giant amplification effect is expected when many molecules are gathered into a small volume like nanoparticles [2]. Herein, we present a negative photochromic molecule from the family of imidazole dimers (Figure 1) [3]. Steady-state and time resolved spectroscopy were carried out to investigate the uncommon photochromic properties of this molecule. The combination with a suitable fluorophore (a BODIPY) was studied in order to promote energy transfer. The molecules were directly gathered into silica nanoparticles or polymer micelles without covalent links. The behavior of the nanoassemblies in these states was investigated to achieve efficient “OFF-ON” fluorescence photoswitching.

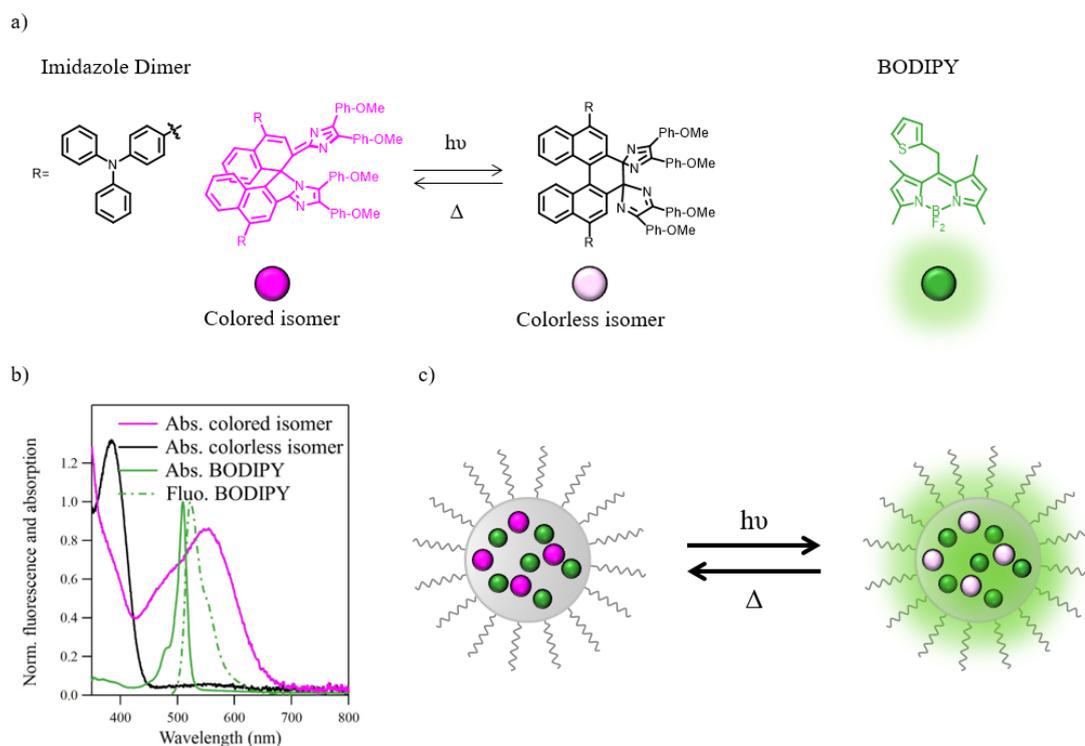


Figure 1 a) Scheme of imidazole dimer isomers and BODIPY derivative, b) their absorption and emission spectra and c) scheme of the “OFF-ON” fluorescence principle in the nanoparticle state.

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Modulating the mechanofluorochromic response of difluoroboron β -diketonates doped polymers by alkyl side chain length

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Among emerging smart materials, mechanofluorochromic ones are promising for force sensing since they exhibit fluorescence modifications under external mechanical stimuli. ^[1] Difluoroboron β -diketonate (DFB) derivatives are well known for their intense solid-state fluorescence and their mechanofluorochromic behavior. ^[2] A series of three DFB designed with different alkyl side chain lengths (DFB-methyl, DFB-butyl and DFB-hexyl, figure 1a) were synthesized in two steps. Their fluorescence properties were studied both in solution and solid state and the as-synthesized powders exhibited a large bathochromic shift of the fluorescence upon grinding.

Polyethylene (LLDPE) polymer films doped with these DFB were then prepared by solution casting. ^[3] The resulting polymer composites were qualitatively submitted to stretching and shearing stress and showed distinct ratiometric mechanofluorochromic responses to these stimuli, with an intensity that depends on the alkyl chain length. A subsequent observation of the polymer samples under the microscope revealed different aggregates sizes of the three DFB in the LLDPE host matrix. Hence, the mechanofluorochromic response of DFB/LLDPE composites can be tuned by varying the length of alkyl side chains and consequently their aggregation mode into the host matrix. Preliminary quantitative experiments to estimate their sensitivity to stretching and shearing stress were performed in order to evaluate their potential use as mechanical stress sensors.

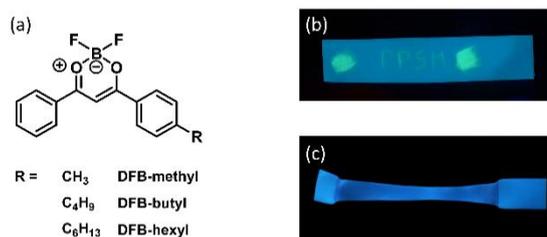


Fig. 1 (a) Structure of the DFB derivatives, pictures of DFB-butyl/LLDPE polymer samples (under irradiation at 365nm) submitted to (b) scratching and (c) stretching.

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Magnetic skyrmions in Dzyaloshinskii-Moriya multilayers and nanostructures

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Magnetic skyrmions are localized spin textures hosted in magnetic films, behaving as individual particles, and topologically different from a uniform ferromagnetic state [1]. In particular, they arise in metallic magnetic multilayers, where they can be stabilised by a subtle balance between the Heisenberg exchange interaction, the interfacial Dzyaloshinskii-Moriya interaction (DMI) – its antisymmetrical exchange analogue, which favours a unique sense of magnetization rotation – and the perpendicular magnetic anisotropy, which defines a main direction for the magnetic order.

Magnetic skyrmions in multilayers were identified to be extremely promising for applications in nano-electronics, enabling a convenient realization of shift-register memories or nano-oscillators [2], as well as for their fundamental interest, e.g., for studying Brownian diffusion properties in magnetic systems [3] or the thermal stability of topological magnetic textures [4]. The magnetism community thus undertook a great effort during the last years to control skyrmion properties, notably their size, velocity, and stability against field and temperature. The mechanisms allowing for an enhancement of the DMI, appropriate for many purposes and uses of skyrmions, are sought after [5]. In particular, we unravel a strong correlation between the work function difference at the interfaces and the amplitude of the DMI [6].

We also aim to briefly introduce the shortcomings of the material systems presently used for the control and manipulation of skyrmions including, more specifically, the identified challenges regarding their electrical detection [7], the limited thermal stability at the single-digit nanometre scale [8], and the detrimental role of device imperfections causing a pinning under current-induced motion [9].

We will finally discuss the prospects for generating skyrmions in two-dimensional crystals and their heterostructures [10]. Based on physical mechanisms identical to those in magnetic multilayers, the realization of skyrmions in stackable van der Waals heterostructures could offer a unique opportunity to lift outstanding issues in the area of skyrmion control and manipulation, owing to their atomically flat and perfect crystalline ordering.

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Dye Alizarin as negative electrolyte for aqueous redox flow battery

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Since the 2000's, the technology of redox flow batteries has been in constant evolution. These systems produce powers of a few hundred kilowatts and can develop in a sophisticated arrangement a power of the order of megawatt with an operating time of up to ten hours. Last results position them favorably to be coupled with the production of renewable energies by playing a buffer role in the energy distribution. Nevertheless, the current systems are based on few redox couples from ores and some of them are highly toxic (vanadium, chromium) [1]. To overcome this problem, a new design of redox flow batteries that use organic redox molecules has recently emerged [2]. Among numerous organic compounds, anthraquinone and its derivatives seem to be very promising owing to their properties.

In this work the commercial dye 1,2-dihydroxy-9,10-anthraquinone, also known as Alizarin, is used as negolyte versus potassium ferrocyanide as posolyte in alkaline medium. This compound presents a good solubility in alkaline aqueous solutions and a suitable potential (-0.93 V in aqueous KOH vs Ag/AgCl) leading to a 1.18 V theoretical cell voltage with potassium ferrocyanide. This negolyte exhibited a very high stability and good performances in battery mode. This molecule presents a high capacity retention compared to other DHAQ (2,6-DHAQ 99.9 %/cycle AQ18OH 99.88 %/cycle) [3] [4].

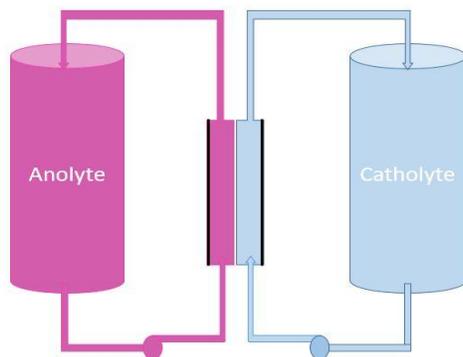


Figure 1: Schematic representation of a redox flow battery

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Impact of nanodiamonds' surface chemistry on their radical overproduction under ionizing radiation

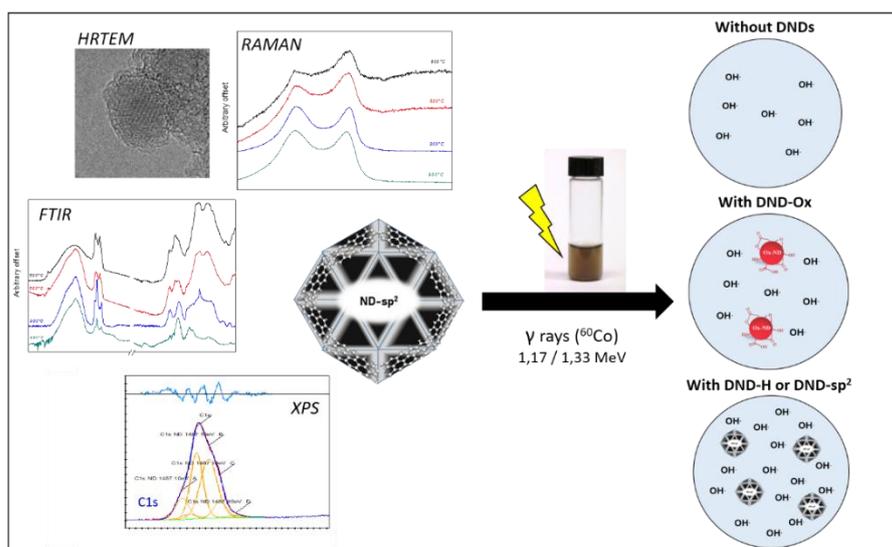
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Within the variety of carbon nanoparticles, nanodiamonds present interesting chemical and physical properties for a wide range of applications^{1,2,3}. Among the different synthesis processes of diamond nanoparticles, detonation nanodiamonds (DNDs) present a mean size of 5 nm suitable for interface studies. We previously demonstrated that under ionizing radiation (X- and gamma-rays), hydroxyl radicals (HO•) and solvated electrons (e_{solv}^-) are overproduced by the presence of hydrogenated DNDs (DNDs-H) in water^{4,5}. These transient species constitute powerful chemical oxidizing and reducing agents that open the way to new applications, especially in photocatalysis (CO₂ reduction into exploitable compounds) or in nanomedicine (radiosensitization of cancerous cells). Surface chemistry appears to be of primary importance since no overproduction was measured for DNDs with an oxidized surface (DNDs-Ox). Furthermore, Raman and HRTEM investigations revealed the presence of some sp²-C content on DNDs-H. These observations question the roles of graphitic reconstructions and hydrogen terminations in the overproduction of HO• and e_{solv}^- . In order to bring new insights on this radiosensitization property, a systematic study of DNDs' graphitization was conducted by annealing under different atmospheres (vacuum and argon) at several temperatures (from 800 to 950°C). The hydrogen and sp² content of each sample (DNDs-sp²) were determined through complementary physico-chemical techniques (FTIR, Raman, XPS, HRTEM) and their colloidal properties were also evaluated. These new samples should then be used for further radical overproduction exploration.



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Modeling Reactivity At The Solid/Liquid Interface:

Are We There Yet?

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To describe reactions occurring at the solid/water interface is currently one of the major challenges in modeling in Heterogeneous Catalysis, especially in the context of biomass valorization.[1] It requires a proper depiction of the water solvent together with an adequate description of the surface state. Several approaches are available nowadays in the literature, from continuum models to a full explicit description of the liquid water.[2] When H-bonding between the liquid water and the reactant or intermediate is crucial, continuum models are not sufficient and an explicit inclusion of water molecule is a necessity. As a first step, micro-solvation can be an effective approach that allowed us to interpret solvent effect in the conversion of levulinic acid into γ -valerolactone.[3] Moving to a full description of reactivity the water/metal interface is still beyond a full complete DFT approach provided the minimal size of the periodic cell that is necessary and the minimal sampling required. A combined QM/MM approach could be a promising strategy,[4] but necessitates a new generation of metal/water force field.[5] Nevertheless, being less demanding, inspecting transformations occurring at oxide/water interface is now reachable, as illustrated by our recent work on the stability of γ -alumina in water. After a fine characterization of the interfacial water[6], we located the weak spot on γ -alumina by a combination of experimental reactivity of shaped-controlled crystals and metadynamics simulations and finally provided a rational for the greatest stability in presence of C5 and C6 polyols.[7]

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From polymer/metal hybrid materials' interface analysis to ToF-SIMS tandem MS measurement optimization.

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To address the ongoing problem of climate change, the transport industry is seeking ways to reduce energy consumption, hence decreasing pollution emissions. At the same time, the biomedical industry is looking for more biocompatible materials, in order to design new implants or prosthesis. To tackle these two different issues, the use of hybrid materials, especially hybrid polymer-metal assemblies, is gaining more and more popularity. Nonetheless, assembling such different materials remains a challenge. From the three assembling techniques, only welding offers satisfying results. Amongst the high variety of welding techniques, laser welding is catching more and more attention. Indeed, the laser welding process is quick. It does not require any surface preparation, and can be easily automated, which further increases its speed. It also presents a high design freedom in size but also in form. Even if laser welding is a promising technique, the root causes of adhesion are still not completely understood. This work aimed at addressing this question by analyzing two combinations of materials: polyamide-6.6/aluminum, and polyamide-6.6/titanium, by combining XPS and ToF-SIMS measurements [1].

ToF-SIMS is an excellent tool for surface chemical characterization, and has been recently adapted to perform tandem MS measurements [2,3]. Therefore the ionization of heavier fragments becomes crucial, especially when analyzing biological or polymeric samples. The use of matrices is one way to increase the total ion yield, as well as the ionization, hence the intensity, of the fragments of interest. The applicability of matrices commonly used for MALDI has already been demonstrated as efficient for biological samples [4], but their use for OLED materials has never been reported. The goal is to optimize the use of matrices for OLED materials in ToF-SIMS measurements, which will help to better understand the ageing of these devices and so possibly help to increase their time of life. Therefore several classical matrices are tested on references of the different OLED layers, in order to find the best fitting matrix.

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Magnetic Molecularly Imprinted Polymer for Cancer Therapy

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Research in nanotechnology prospered during the last decade and yielded several prerequisites for drug delivery systems. Among the broad spectrum of nanoscale materials being investigated for biomedical applications, magnetic nanoparticles (MNPs) have attracted significant attention due to their intrinsic magnetic properties. The last 20 years have witnessed an important increase in the number of reports dedicated to magnetic hyperthermia [1]. Magnetic hyperthermia is a type of thermal cancer treatment that takes advantage of the heat generated by magnetic nanoparticles when applying alternative magnetic field (AMF). An interesting field of research concerns the use of localized temperature around the magnetic nanoparticles (hot spot effect). The imprinting process involves the polymerization of a functional monomer in the presence of a molecule with a cross-linking agent. After the extraction of the molecule, the polymer matrix contains tailor-made binding sites, perfectly complementary to the molecule. The synthesis of molecularly imprinted polymer (MIP) is reproducible, fast and economic. MIPs have been widely utilized as molecular-recognition and separation materials in different fields. In recent years, their use in nanomedicine has emerged [2]. In this context, we recently developed an innovative molecularly imprinted polymer (MIP) magnetic delivery nanomaterial for triggered cancer therapy showing active control over drug release using AMF [3]. Upon AMF, the magnetic nanoparticle locally heats and the drug, sequestered in the MIP, is released by disrupting hydrogen bonds existing with the polymer. We recently demonstrated the same behavior with inorganic imprinted polymers i.e., silica [4]. After 1h30 AMF application, cancer cell viability is reduced to 60% in athermal conditions while the control cells do not suffer any mortality (Figure 1). As many anticancer drugs possess side effects, this novel material could be helpful to release the drug, with control, at the desired place.

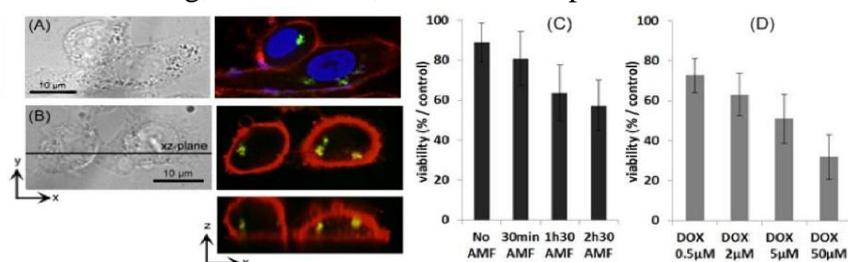


Figure 1. Prostate cancer cells (PC-3) internalization of the magnetic MIP nanoparticles containing DOX. (A) DOX is detected in the green channel, nuclei and cell membranes are stained by DAPI in blue and PKH26 in red. Z reconstructions (B) identify DOX in cells. (C): Viability of cancer cells labelled with magnetic MIP containing DOX after exposure to AMF compared to the control experiment. (D) Treatment of cancer cells with DOX for 2 hours.

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MOLECULAR DESIGN FOR CATALYTIC ACTIVITIES OF HELICAL CHIRAL OLIGOUREAS

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Abstract

The use of organocatalysts to achieve challenging asymmetric transformations with low catalyst loadings has recently gain attention as an alternative to metal-based catalysis. On this direction, Bécart et. al. [1] have demonstrated the use of bioinspired urea-based foldamers as robust alternatives, able to catalyze C-C bond forming reactions with loadings as low as 1:10000 catalyst/substrates. They found, increasing the size of the foldamer (see fig.1) from one to nine residues, that its reactivity and enantioselectivity have a peak around pentamer and hexamer, what suggests that there is a minimum and maximum number of residues allowed to obtain the expected results. This theoretical investigation, using B3LYP and the 6-31G(d,p) basis set, aims to rationalize the influence of the foldamers on the malonate ester and nitroalkenes C-C bond forming reactions (see fig.1). We have found that the first two ureas are the only H-bond donors available to interact with external molecules, because from the third urea onward they are exclusively used to achieve the foldamer's helicoidal shape. Moreover, it has been observed that the molecular recognition and catalyst-substrates interactions are not mainly governed by orbital interaction but by electrostatic interactions. Following that hint, an electrostatic potential (ESP) analysis showed an important internal charge separation [2] in the catalyst, being the positive ESP region concentrated around the first two ureas, extending its area as the number of residues augments. These results explain the way the substrates arrive at the foldamer, and it favorable effect on their molecular orbitals to the reactions to take place.

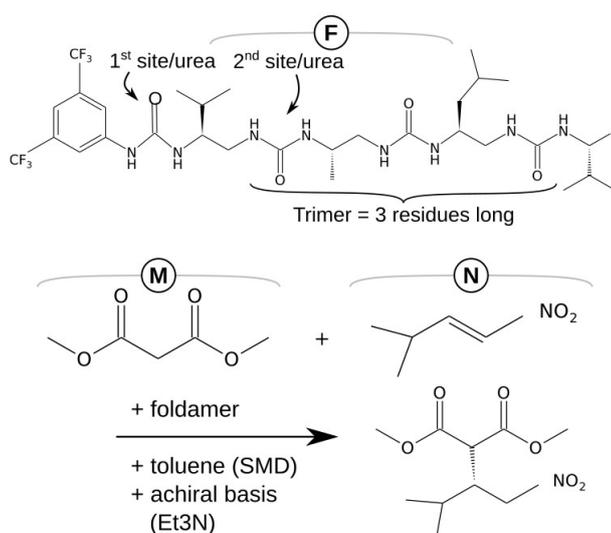


Figure 1. Foldamer (F) presentation and description, along with the malonate ester (M) – nitroalkene (N) C-C bond forming reaction under study in our investigation.

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Multi-basis-set TDDFT methods for predicting electron attachment energies

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Understanding the interaction of low-energy electron collisions with molecules constitutes a key subject in a large area of fundamental research as well as modern applications in various fields of science such as astrochemistry, radiation-induced damage of biological tissue, selective chemistry, or chemical synthesis at nanoscale.

Collision of a low energy electron with a molecule can induce various phenomenon such as dissociation, ionization, isomerization, reactivity, etc, through the formation of a transient negative anion composed of the target molecule and the projectile electron, that can evolve toward a dissociative state through selective phenomenon.

A complete theoretical characterization of the temporary anion, which would describe the electron attachment, the relaxation of electronic and vibrational degrees of freedom, and possible fragmentation processes, is still challenging. Limitations come from the difficulty to treat the electron correlation in an anionic system, the need to combine continuum and discrete states, and the high number of degrees of freedom, which make the numerical calculation very cumbersome.

Among the most popular computational methods for describing temporary anions¹, one can find a broad class of methods that compute the electron attachment energies, such as the R-matrix², the so-called empirical correlation method³, the Schwinger multichannel method⁴, or the stabilization method⁵. Although these methods provide valuable results, they rely either on cumbersome calculations or on empirical methods.

Here, we propose an efficient approach to predict the resonance energies of the electron attachment using a TDDFT calculation and two different atomic basis sets⁶: a large basis set to compute the vertical electron affinity, and a smaller one to calculate the excitation energy of the anion. Doing so one computes the relevant resonant attachment energies of the electron without intruder states from the continuum discretized due to the finite size of the simulation box. Benchmarks have been performed over 18 molecules and 53 resonances and show good agreement with experimental data.

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PAHs on metallic surfaces: from the adsorption to electron-stimulated processes

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Polycyclic aromatic hydrocarbons (PAHs) correspond to organic compounds with two or more fused aromatic rings. They are among the most investigated and interesting molecules as their studies span from astrochemistry to nanotechnology or spintronics. PAHs are found to be abundant in interstellar space and to represent a not negligible part of the composition of the dust in the diffuse interstellar medium. Moreover, the adsorption of neutral PAHs is studied as a prototypical case of organic precursors with the aim to form new architectures with specific dimensions and geometry, as in the case of the formation of graphene and graphene-derived structures. It has been shown that the chemistry and reactivity of PAHs is of valuable for the synthesis of graphene sheets or nanoribbons, which is of particular interest for nanoelectronics and spintronics. Finally, PAHs adsorbed on relatively inert substrates constitute template molecules or systems for the development of theoretical calculations, and more especially in the framework of van der Waals density functional theory. From the above reasons, it appears clear that understanding the reactivity of PAHs and their derivatives, as well as their on-surface behavior, is of particular importance due to their potential implication in different research fields.

In this work we focus our attention on different physical-chemical processes of pyrene molecules on metallic surfaces (Ag(111) and Cu(111)). We first demonstrate that despite its high vapor pressure, pyrene molecules can form ordered films under ultra-high vacuum conditions, presenting a well contrasted diffraction pattern. Studies using high-resolution electron energy loss spectroscopy and ultra-violet photo-electrons spectroscopy provide compelling evidence of a physisorbed system where the molecules only poorly interact with the underneath substrate. Comparisons with theoretical calculations, as well as with data obtained from optical spectroscopies, clearly demonstrate that the vibrational and electronic properties of the adsorbed molecules are similar to the expected ones for pristine pyrene. Moreover, we used temperature-programmed X-rays photo-electrons spectroscopy to study the desorption process of the pyrene on metallic surfaces and estimate its desorption energy [1]. Eventually, we present preliminary results on electron-stimulated processes of pyrene and pentacene adsorbed on Ag(111) and Cu(111), in particular focusing on the surface processes induced by low energy electrons (4-20 eV).

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Revisiting HER on MoS₂: The impact of water and the electrochemical potential

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MoS₂ is a promising low-cost catalyst for the hydrogen evolution reaction (HER). However, the nature of the active sites remains controversial¹. By explicitly considering the electrochemical potential using grand canonical density functional theory (DFT) in combination with the linearized Poisson-Boltzmann equation², we revisit the active sites of 2H-MoS₂. We start with the edges and we assess the influence of the presence of water and the competition between the release of H₂S and H₂. In our calculations, we consider the 50% S-edge and the 50%S Mo-edge, as they have been shown to be the most stable edge structure. Our calculations reveal that the Mo-edge is very likely to be reconstructed in the presence of water. In particular, H₂S formation is only weakly endothermic (0.4 eV). Hence, under HER conditions where there is no sulfur reservoir, sulfur is gradually replaced by oxygen. Fortunately, the 0%S Mo-edge covered by OH is active for HER, as shown in our previous study³. For the 50% S-edge, the termination is more stable with respect to H₂S release (2.5 eV) and OH is stably adsorbed on the Mo-Mo sites. Our grand canonical DFT computations suggest that this edge is active for HER. The release of H₂S at this edge is less likely to take place compared to H₂ generation but is still possible as it is endothermic by only 0.21 eV after adsorption of OH. Once this OH substitutions happen, it leads to a 0%S S-edge that is predicted to be inactive for HER. For the basal plane, the thermodynamics of proton reduction as a function of electrochemical potential shows that three basal plane defects exhibit thermodynamic overpotentials below 0.2 V³ and the single sulfur vacancy (Vs) is the most abundant defect. Therefore, we present a detailed mechanistic study of HER on this defect and evaluate the Volmer, Tafel and Heyrovsky transition states for the different possible reaction steps by considering the activation energy as a function of the electrochemical potential.

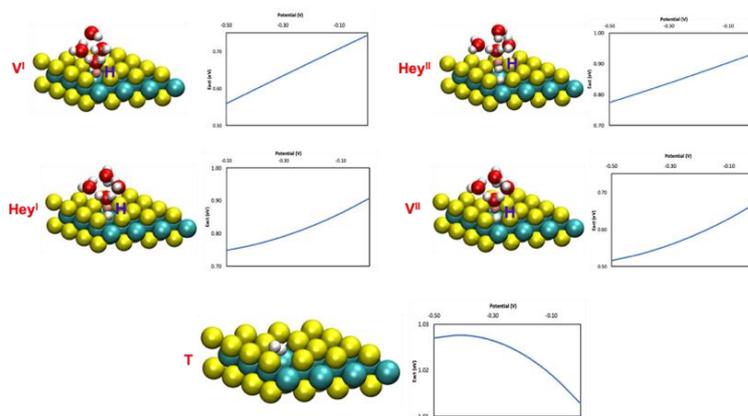


Figure 1: The different possible steps to produce H₂ on the single sulfur vacancy (Vs)

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Structural study of ionic liquid aggregates in an aqueous biphasic system using small-angle neutron scattering.

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Phase separation in an aqueous biphasic system is the result of subtle balance between entropy and enthalpy of the system, both varying with temperature. It is highly dependent on the systems, and not clearly understood yet. In order to get more insight into the driving mechanisms of the phase separation, microscopic structural investigations are invaluable information. Small-angle neutron scattering (SANS) techniques are suited for the study of both micro and mesoscopic organisations and have been used to highlight the formation of spherical micelles of ionic liquid (IL) in aqueous solutions[1]. By contrast, very little studies have been done on that subject for aqueous biphasic solutions (ABS) where acid is added to the IL and the water, apart from evidence of similar aggregation behaviors in the IL-rich upper phase[2]. SANS measurements were performed at the ISIS and the ILL neutron sources on ABS samples to study IL micelles form and structure, using P44414Cl ionic liquid along deuterated nitric, hydrochloric and sulfuric acids. The micelles have been found to be cylindrical with a radius around 15 Å similar to the radius of the spherical micelles formed in acid free solutions and a variable length ranging from 50 Å to 1500 Å depending on the acid type, the acid concentration and the solution temperature. The change in the self-aggregation behavior of the ionic liquid as a function of the latter parameters is discussed and correlated to the phase separation phenomenon.

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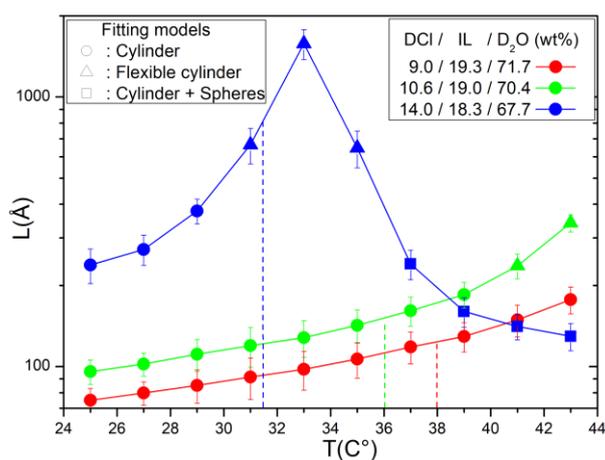


Figure 1 : Cylindrical micelles length evolution as a function of temperature for three hydrochloric acid based ABS.

Tailored solutions targeting specific pollution problems

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Constant environmental monitoring and pollution control have become imperative, as the environment pollution has tremendously increased due to rapid modernization and industrialization. Two important pollution problems are addressed in this work.

Corrosion of metals leads to the deterioration or even to the complete collapse of a range of materials used in infrastructure works. On top of economic effects, the deterioration of metal-based materials can be the source of the release of polluting compounds in the environment. Magnesium-based swimmers, capable of cooperative chemotaxis movement, are used to spot localized corrosion events on an iron rod. Following a basic pH gradient, the swimmers aggregate and move in an autonomous manner towards the site of corrosion. The newly formed cluster docked at the active corrosion site can be used as a direct visual detection (**A1**). Upon contact with iron, Mg swimmers start to create a magnesium hydroxide layer on the surface of the iron. This layer increases the resistance to corrosion (**A2/A3**) [1].

Air pollution is another important environmental problem that is tackled in our research. The detection of harmful gases, like ammonia, has become crucial, for the protection of the atmospheric environment and human health. Conducting polymers are suitable candidates for gas sensors as their chemical, electrical, and structural properties can be easily tunable [2]. Metal-macrocycles can favor electron transfers between the sensor and the gas analytes. The electrochemical incorporation of two types of phthalocyanines (sulphonated and non-sulphonated) into multilayer conducting polypyrrole film was performed onto FTO electrodes in aqueous solution, in the presence of two types of surfactants (cationic surfactant- Cetyltrimethylammonium bromide and anionic surfactant -Sodium dodecyl sulfate). The structural aspect and the thickness of the films, important characteristics for the gas sensing, present well described and controlled variations.

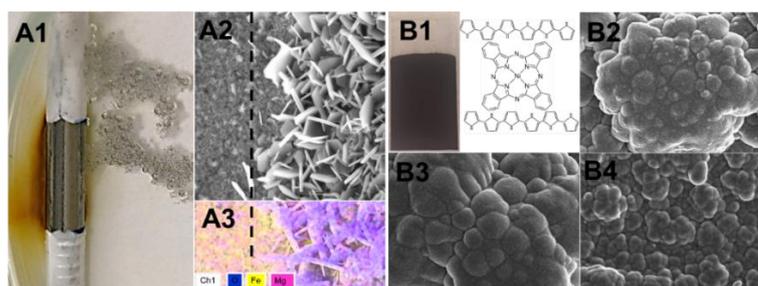


Figure. **A1** Mg swimmers docked at the corrosion spot. **A2/A3** SEM/ EDS maps of the corrosion protecting layer, **B1** FTO/ metal polymer and its scheme, SEM micrographs of metal polymer films in the absence (**B2**) and in the presence of CTAB (**B3**) or SDS (**B4**)

This work is supported by the European Union through the fonds Européen de Développement Régional (FEDER), and the Regional Council of Bourgogne Franche-Comté through the PIA-excellence ISITE-BFC program CoMICS: Chemistry of Molecular Interactions Catalysis and Sensors, and by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no 741251, ERC Advanced grant ELECTRA).

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Ab-initio Study of CD and CPL properties of lanthanide complexes

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Since the pioneering work of van Vleck,[1] it is well established that crystal field splitting is at the origin of both magnetic and luminescence properties in lanthanide-based complexes and consequently both properties are strongly correlated. In parallel, there is a growing interest in the use of circular dichroism (CD) and circularly polarized luminescence (CPL) for the characterization of electronic structures in chiral lanthanide-based complexes. However, the interpretation of CD and CPL spectra of such systems is by far not straightforward, principally because of their rather complex electronic structures arising from partially filled valence shells. These systems are also very challenging for quantum chemistry due to (i) the presence of degenerate electronic states with multi-configurational character and (ii) the importance of the spin-orbit coupling in the calculations of the spin-forbidden transitions. In this talk we will present our recent results on the ab-initio calculations of CD and CPL parameters on series of complexes containing either europium or ytterbium centers.[2,3]

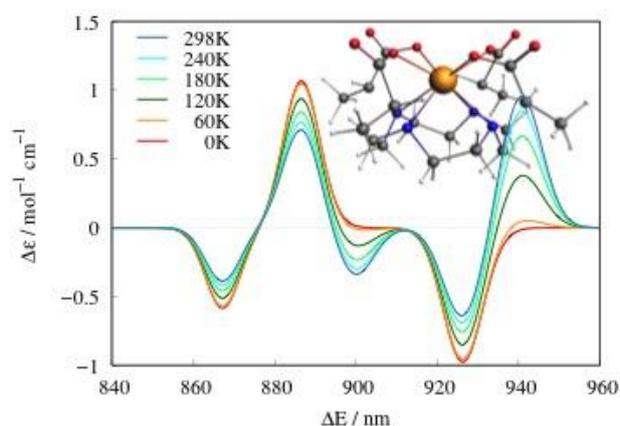


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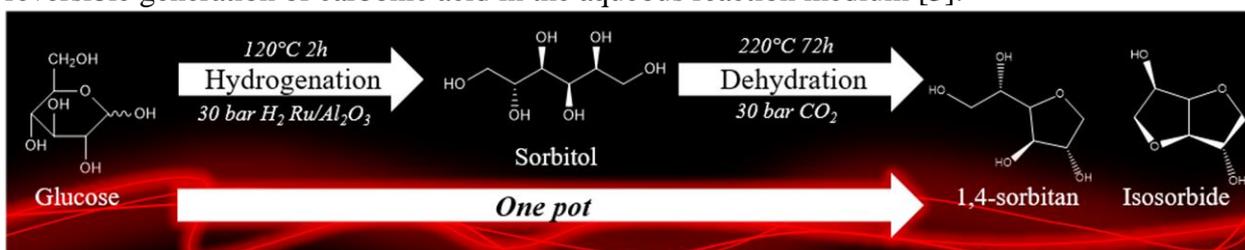
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***In situ* IR Spectroscopy and DFT calculations for the insight of the CO₂-assisted conversion of glucose into isosorbide**

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Environmental concerns aim to develop molecules from sustainable biomass resources to substitute petro-sourced raw material. Bio-sourced isosorbide is considered as a relevant alternative to several conventional petro-sourced diols as it can be used in a wide range of applications like plasticizers, solvent and pharmaceuticals. The isosorbide synthesis is a two-step process starting from 1) the catalytic hydrogenation of glucose to sorbitol followed by 2) the sorbitol dehydration into (di)anhydro-sorbitans assisted by mineral acids (HCl, H₂SO₄) [1]. In view of the toxicity of this last step and purifications processes that it implies, greener protocols should be proposed. In this context, the aim of this study is two folds: 1) investigate the *one pot* isosorbide synthesis directly from glucose [2] in order to reduce isolation and purification procedures, 2) replace toxic mineral acids used for the acid-catalyzed dehydration step by gaseous CO₂ for the reversible generation of carbonic acid in the aqueous reaction medium [3].



The two steps of the reaction were firstly studied separately and optimized by using batch reactors. Glucose was hydrogenated into sorbitol in the presence of a commercial Ru/Al₂O₃ catalyst and gaseous H₂ in aqueous media. Sorbitol was selectively obtained at optimal conditions (100°C-2h30) and Ru/Al₂O₃ was recyclable up to 10 cycles showing its unexpected stability in water [4]. Then, sorbitol was dehydrated into 1,4-sorbitan and isosorbide in the presence of gaseous CO₂ in aqueous media. The higher selectivity towards the formation of 1,4-sorbitan under selected conditions (220°C-72h) was rationalized by DFT calculations that were done to compare the catalytic effect of carbonic acid and hydrochloric acid in the reaction mechanism of sorbitol dehydration. Consecutive hydrogenation and dehydration starting from glucose were then studied in a *one pot* process. Unfortunately, a systematic drop in the reaction yield and selectivity was observed under the optimized conditions for the two steps process. Thus, the effect of gaseous CO₂ on the hydrogenation step was investigated by *in situ* and *in operando* IR spectroscopy in order to identify side effects generated by the *one pot* protocol.

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Novel Arene Ru(II) complexes derived from cis-2,2'-Azobispyridine and their behavior under light or electron stimulation

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Azopyridine is a well-known photochromic organic compound that can act as ligand for metal center.^[1] Linear patterns such as **I** and **II** are most common for 4,4'- and 3-3'-azobispyridine while bidentate or tridentate coordination mode with 5-membered chelate rings such as **IIIa** or **IIIb**, are found with *E*-2,2'-azobispyridine (Figure 1, left). A peculiar property of the latter ligand in these systems is that it usually does not undergo *E-Z* photo-isomerization. To the best of our knowledge, metal complexes of type **IV** involving coordination of the two nitrogen atoms of the pyridine rings of *Z*-2,2'-azobispyridine, suggested by Baldwin as early as 1969, have never been reported so far.^[2]

In this work, we report the synthesis of novel arene Ru(II) complexes derived from 2,2'-azobispyridine, notably exhibiting an unprecedented *Z*-configured 7-membered chelate ring with the metal center. Their behavior in response to light or electrons will be detailed with absorption spectroscopy, electrochemistry, NMR spectroscopy, DFT calculations and X-Ray diffraction studies. (Figure 1, right).^[3]



Figure 1 Left: Common coordination pattern exhibited by azobispyridine (**I**, **II**, **III**) and a novel 7-membered chelate ring described in the present study (**IV**). Right: Photo/Electro-induced irreversible isomerization of Ru complexes bearing 2,2'-azobispyridine ligand with concomitant rearrangement of the coordination pattern of the ligand.

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Biomimetic approach for highly selective artificial water channels based on tubular Pillar[5]Arene dimers and trimers

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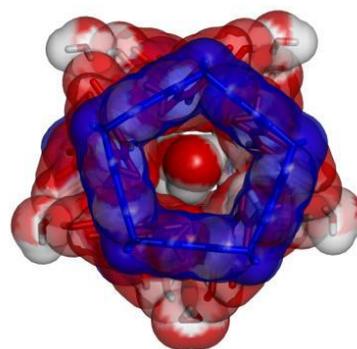
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Nature provides answers for efficient transport of water by using Aquaporins AQPs as the translocation relays. Artificial Water Channels biomimicking natural AQPs, can be used for both selective and fast transport of water. Here, we use complementary synthetic methods, X-ray structural data, transport assays to quantify the transport performances of peralkyl-carboxylate-pillar[5]arenes dimers in bilayer membranes. They are able to transport $\sim 10^7$ water molecules/channel/second, within one order of magnitude of AQPs' rates, rejecting Na^+ and K^+ cations. The dimers have an tubular structure, superposing larger pillar[5]arene pores of 5 Å diameter with narrowest twisted carboxy-phenyl pores of 2.8 Å diameter. This exceptional channel biomimetic platform, with variable pore dimensions within the same structure, offers size restriction reminiscent to natural proteins. It allows water molecules to selectively transit and prevent bigger hydrated cations to pass through the 2.8 Å pore. Molecular simulations probe that dimeric or multimeric honeycomb aggregates are stable in the membrane and form water pathways through the bilayer. Over time, a significant shift of the upper vs. lower layer of occurs initiating new unexpected water permeation events through novel toroidal pores. Altogether, uncovering the interplay between supramolecular construction and transport performances, the novel PAD channels described here are critical to accelerate the systematic discovery for artificial water channels for water desalting.



Keywords: Artificial water channels, pillar[5]arene, aquaporins, bilayer membranes

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Protein imprinted polymers targeting CD36 overexpressing cells and magnetically-triggered drug release

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The molecular imprinting technique allows the formation of cavities inside a polymer matrix that have a specific affinity for a chosen “template” molecule. The resulting molecularly imprinted polymers, sometimes referred as “synthetic antibodies”, are versatile materials offering recognition properties similar to those of natural antibodies while exhibiting an increased stability with lower manufacture costs. The possibility to imprint surface proteins that are overexpressed on cancer cells, such as fatty acid transporter CD36, enable a specific targeting of cancer cells. The encapsulation of a drug inside the polymer matrix would create a powerful drug delivery system with the ability to specifically target certain types of cells. In order to control the drug release, we combine molecular imprinting with superparamagnetic iron oxide nanoparticles, possessing magnetic hyperthermia properties, to trigger the drug release by applying an alternative magnetic field (AMF). The local heat generated around iron oxide nanoparticles by the AMF breaks weak interactions between the drug and the polymer. We hereby aim to design a hybrid material with an iron oxide core exhibiting specific affinity for CD36 and encapsulating a drug.

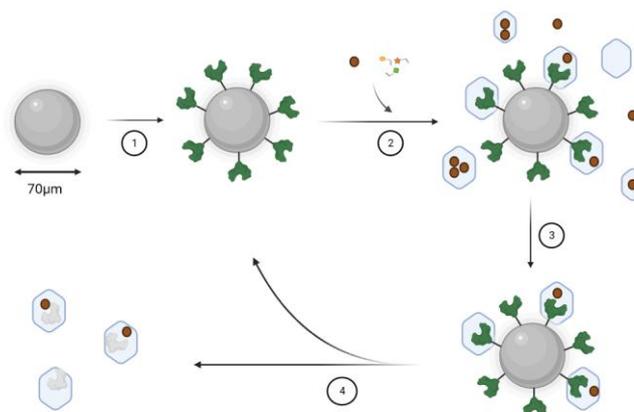


Figure 1 Magnetic protein imprinted polymer solid phase synthesis technique[1]. (1) Glass bead functionalization with CD36 epitope. (2) Polymerisation induced through UV irradiation with a monomer mixture in presence of magnetic iron oxide nanoparticles. (3) Cold washing to eliminate unreacted monomers and non-specific nanoparticles. (4) Warm washing, freeing specific nanoparticles by breaking weak interactions.

Study of the kinetic reactions of formate dehydrogenase within an electrode.

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In nature, there are different types of enzymes that catalyze specific reactions. For example, formate dehydrogenase (FDH) is an enzyme capable of catalyzing CO₂ to formic acid [1]. It is also possible to produce methanol from CO₂ by cascade reactions with specific enzymes [2, 3]. However, enzymatic reactions require an electron and proton donor coenzyme to work. Generally, nicotinamide adenine dinucleotide (NADH) is the coenzyme used in these enzymatic reactions.

Moreover, enzymatic reactions are catalytic reactions. If we can increase the enzymatic active surface through a better design of the electrode, we could then promote the electro-reduction of CO₂. Thus the objective of the FAME project is to manufacture membrane electrode assemblies with enzymes by mimicking PEMFC (Proton Exchange Membrane Fuel Cell) technology to promote the electro-reduction of CO₂.

In this work, our first attempt is to study the FDH activity with and without immobilization within a support in carbon felt by studying the kinetic reactions described by equations (1) and (2). According to literature [2, 3], the enzyme activity is defined and measured through equation (1), however the consumption of CO₂ (in equation (2)) is the goal of our project. Here, we have tested two types of electrodes (Figure 1), where the binder is embedded inside the support or only on the surface.

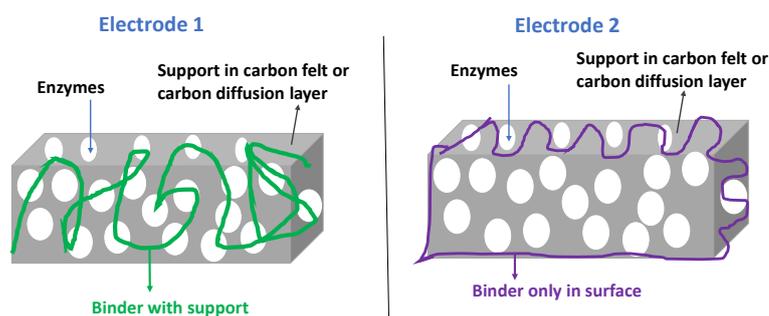


Figure 1: Schema of enzyme immobilization

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This project is supported by MITI CNRS project (FAME) 2021.

Thermo-mechanical Properties of Various Epoxy-Amines Resins: Insights from Molecular Simulations

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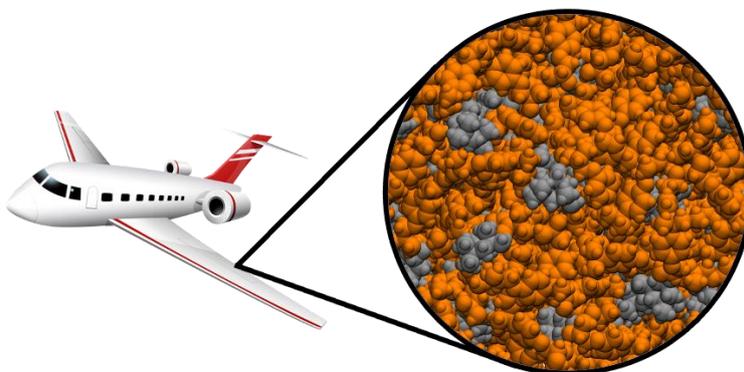
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Epoxies are some of the most prominent thermosetting polymers valued nowadays due to their wide range of applications. This class of polymers is of interest for instance for structural components in aerospace applications as well as electronics packaging or various types of coatings. This is made possible by their interesting versatility. The final material can be easily modulated by the chemical structure, then responsible for its striking thermal and mechanical properties.

Therefore, it is of great importance to be able to characterize them and comprehend the influence of the structural network on their properties. Aside from the usual experimental testing, computational chemistry has shown to be a great asset to this task, in particular by using molecular simulations. [1]

In the scope of this project, all-atom molecular dynamics performed on Lammmps with the CHARMM force field were used to characterise various epoxy resins, such as aliphatic or bisphenol-based ones. A multi-step crosslinking algorithm as well as several methodologies to obtain key properties, such as density, glass temperature, and elastic modulus, were designed. A quantitative comparison was made and was proven to be in good agreement with experimental data.



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