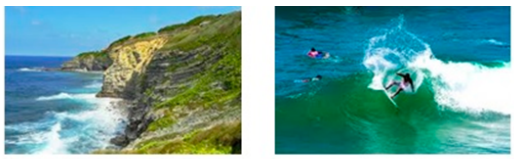

Rencontres de Chimie Physique 2019

6-9 octobre - Domaine de Françon - Biarritz

https://rcp19.sciencesconf.org/

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INTRODUCTION

La Division de Chimie Physique et le comité d'organisation ont le plaisir de vous accueillir à Biarritz pour les Rencontres de Chimie Physique 2019.

Ces rencontres annuelles sont organisées sous l'égide de la Division Chimie Physique, commune à la Société Chimique de France (SCF) et la Société Française de Physique (SFP) avec, pour cette édition 2019, le concours de la section Aquitaine de la SCF.

L'objectif principal de ces journées est de rassembler la communauté des physico-chimistes (juniors et séniors) et d'échanger autour des résultats scientifiques dans les domaines couverts par la DCP. Des conférences plénières seront données par des personnalités scientifiques reconnues dans les différents domaines de la physico-chimie, et par les lauréats des Prix de thèse, du Prix Jeune Chercheur.e, du Chercheur.e Confirmé.e, du prix d'instrumentation de la DCP et du Prix Jeune Chercheur.e de la SFP.

La conférence Jean Perrin 2019 est donnée par Hélène Budzinski (DR CNRS), internationalement reconnue dans le domaine de la chimie analytique appliquée à l'étude de l'environnement.

Les sessions seront organisées autour des thématiques des subdivisions :

Chimie Analytique

Chimie Sous Rayonnement et Radiochimie

Electrochimie

Magnétisme & Résonance Magnétique

Modélisation & Simulation

Nanosciences

Spectroscopie Optique et Neutronique

Photochimie, Photophysique et Photoscience

Nous vous encourageons à participer aux discussions scientifiques et espérons que les RCP19 seront l'occasion d'échanges scientifiques conviviaux et fructueux.

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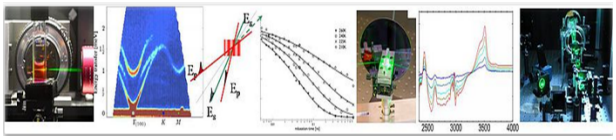

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PROGRAMME DES RCP19

Dimanche 06/10/2019

A partir de 16h	**Accueil des participants**
18h00-18h15	S. Coussan / D. Scuderi (Président /Vice-présidente de la DCP) Introduction aux RCP19
	Sylvie Rousset (vice-présidente de la SFP) Présentation du prix SFP
18h20-18h55	**A. Fargette -** ***Prix Jeune chercheure SFP*** **Une goutte, deux vitesses: la dynamique surprenante d'une goutte d'eau sur un élastomère silicone.**
19h15-20h45	Diner
	Modérateur : Debora Scuderi - Présentation du prix jeune chercheur.e DCP
20h50-21h20	**C. Meinert** (ICN, Université Côte d'Azur) **-** ***Prix Jeune chercheure DCP*** **The Asymmetry of Life**

Lundi 07/10/2019

8h45	*Modérateur : S. Coussan*
8h50-9h35	**H. Budzinski** (EPOC, Université de Bordeaux) **-** ***Conférence Jean Perrin*** **Mieux caractériser les composés "inconnus" dans les mélanges complexes dont les produits de transformation : un enjeu considérable en chimie de l'environnement**
9h40-9h55	S. Labat (IPREM, Université de Pau et Pays de l'Adour) Approche multi techniques pour la caractérisation de carbènes élusifs
10h00-10h15	C. Mongin (PPSM, ENS Paris-Saclay) Innovative Atrazine microfluidic colorimetric sensor based on barbiturate derivatives microcrystals
	Pause
	Modérateur : M. Dussauze – Subdivision de Spectroscopie Optique et Neutronique
10h45-11h20	**P. Simon** (CEMHTI – CNRS Orléans) **-** ***Conférence invitée*** **Diffusion Raman et matériaux du nucléaire: imagerie, *in situ* sous irradiation, et résolution temporelle**
11h20-11h35	V. Dru (CEA) Research of Interactions in U(IV)/U(VI) Mixtures
11h35-11h50	C. Pardanaud (PIIM, Université Aix Marseille) Multi-wavelength Raman microscopy: investigating physico-chemistry on tokamaks walls
11h50-12h05	L. Karam (ISM, Université de Bordeaux) New sodo-niobate amorphous thin films: microscale patterning of strong second order optical response by thermal poling
12h05-12h20	T. Guerineau (ICMCB – CNRS, Bordeaux) X-ray resilient silver-based structures generated by infra-red femtosecond laser: understanding of their origin and formation mechanism
12h30-14h00	Déjeuner
	Modérateur : H. Perrot - Subdivision Electrochimie
14h15-14h50	**E. Lojou** (BIP, Université Aix Marseille) **-** ***Conférence invitée*** **Electrocatalyse enzymatique : pourquoi, comment?**
14h50-15h05	Q. Lenne (ISCR, Université de Rennes) Metallic Nanoparticles Functionalized with Calix[4]arenes as Selective Catalysts for Oxygen Reduction Reaction (ORR)
15h05-15h20	G. Loget ((ISCR, Université de Rennes) Photo-Induced Electrochemiluminescence by Upconversion at Silicon Electrodes in Water
15h20-15h35	A. Dauphin (ISM, Université de Bordeaux) Optical fibers for Confocal Microscopy under Electrochemical control: A case study with electrofluorogenic species
15h35-15h50	M. Alvarez (Laboratoire d'électrochimie moléculaire, Paris Diderot) Halogen Bond and Electrochemistry: A promising cooperation for controlling supramolecular architectures in solution and on surface
	Pause
	Modérateur : E. Maisonhaute - Instrumentation / Nanosciences
16h20-16h55	**E. Levillain** (MOLTECH Anjou , Angers) **-** ***Prix instrumentation*** **SpectroElectroChimie d'Absorption (A-SEC) en temps réel : De la molécule à la monocouche.**

16h55-17h10	M. Tricoire (LCM, Ecole Polytechnique, Palaiseau) Electronic properties of heterobimetallic complexes of lanthanide and transition metal
17h10-17h25	G. Simon (MONARIS, Sorbonne Université) Propriétés vibrationnelles de nanoparticules auto-organisées de cobalt et de coeur/coquille cobalt/oxyde de cobalt
17h25-17h40	S. Tricard (LPCNO, Toulouse) Chemical Tuning of Coulomb Blockade at Room-Temperature in Ultra-Small Platinum Nanoparticle Self-Assemblies
17h40-17h55	F. Carn (Laboratoire Matière et Systèmes Complexes, Paris Diderot) Intracellular Biotransformation of Gold Nanoparticles
18h00 – 19h30	Session poster
	Diner
	Réunion du conseil de la DCP

Mardi 08/10/2019

8h45	Organisateurs - Introduction / Annonces
	Modérateur : R. Métivier - Subdivision Photochimie, Photophysique et Photosciences
8h50-9h20	**T. Gustavsson** (LIDYL, CEA, CNRS, Paris-Saclay) **- *Conference invitée*** **Molécules «push-pull» pour le photovoltaïque étudiées par spectroscopie de fluorescence femtoseconde**
9h25-9h40	C. Carayon (SPCMIB, Toulouse) Mechanofluorochromic properties of an an AIEE-active 2-phenylbenzoxazole derivative: more than meets the eye?
9h40-9h55	C. Jegat (PPSM, ENS Paris-Saclay) Photochromic molecules and plasmonic materials for new reversible switchable devices
10h00-10h15	S. Chevalier (Physique de la Matière Condensée, Palaiseau) Hybrid nanostructured thin films, optically tunable.
	Pause
	Modératrice : C. Allain - Subdivision Photochimie, Photophysique et Photosciences
10h45-11h00	J. P. Calupitan (PPSM, ENS Paris-Saclay) Multi-scale investigation of mechanofluorochromism of a donor-acceptor compound
11h00-11h15	B. Poggi (PPSM, ENS Paris-Saclay) Matériaux mécanofluorochromes : quantification de leur réponse à des stimuli mécaniques
11h15-11h30	O. Soppera (IS2M, Mulhouse) Photopolymerization at the nanoscale controlled by plasmon resonance
11h30-11h45	N. McClenaghan (ISM, Université de Bordeaux) Stochastic energy shuttling in molecular machines and supramolecular systems
11h45-12h00	J. Delazay (ISMO, Université Paris Sud) Excited state dynamics of protonated RNA/DNA bases in a cryogenically cooled ion trap: the case of uracil
12h00-12h15	G. Laurent (PPSM, ENS Paris-Saclay) Influence of the aggregation of metallic nanoparticles when coupled to photochromic molecules in hybrid systems
12h30-14h00	Déjeuner
	Modérateur : P. Larregaray - Subdivision Modélisation et Simulation
14h15-14h50	**M. Alducin** (Materials Physics Center, San Sebastian)- ***Conférence invitée*** **Femtosecond laser-induced desorption of CO on metals: hot electrons and phonons at play**
14h50-15h05	Wang Jin (ICSM/L2IA , CEA Marcoule) Study of the liquid-liquid interface containing an extractant: Experiments and molecular dynamics modelling
15h05-15h20	H. Bessone (Laboratoire PASTEUR – UMR 8640) Quasi-Classical Simulation of Resonant Raman Spectra using Linearization in Molecular Dynamics
15h20-15h35	J. Donnon (LIDYL, CEA, CNRS, Université Paris-Saclay) Identification of ion pairs in solution by IR spectroscopy: crucial contributions of gas phase data and simulations

15h35-15h50	T. Stirnemann (IBPC – CNRS) Abiotic synthesis of RNA: towards an understanding of key molecular steps
	Pause
	Modérateur : B. Le Guennic - Subdivision Modélisation et Simulation
16h20-16h35	C. Latouche (IMN, Nantes) Decipher the role of point defects on the optoelectronic properties of materials: the never ended story of TiS2
16h35-16h50	S. Sarr (CEISAM, Université de Nantes) Astatinated mediated halogen bond in X3C–At…Z- systems
16h50-17h05	X. Michaut (LERMA, Sorbonne Université) Etats de spin nucléaire de l'eau : du confinement extrême en matrice de gaz rare au milieu interstellaire
17h05-17h20	L. Huart (NIMBE - Lions – CEA) Quantifying water ionization by soft X-rays using a microfluidic device
17h20-17h55	**B. Senjean** (Institut Lorentz, Université de Leyde) **- *Prix de thèse de la DCP*** **Site-occupation embedding theory for the treatment of strongly correlated systems**
18h15	Rendez-vous devant l'hôtel – Bus
	démonstration de CESTA PUNTA / Apéritif
	Diner de Gala (Ascain)

Mercredi 09/10/2019

8h45	Organisateurs - Introduction / annonces
	Modérateur : G. Baldacchino - Chimie sous rayonnement et radiochimie
8h50-9h20	**M. Mostafavi** (LCP, Université Paris Sud) **-** ***Prix chercheur confirmé de la DCP*** **Un électron peut-il induire un dommage oxydatif à l'ADN? Etude par la radiolyse impulsionnelle picoseconde**
9h25-9h40	V. Lepere (ISMO, Université Paris Sud) Discrimination chirale au sein de Dicétopiperazines
9h40-9h55	M. Abdelmouleh (CIMAP, Caen) Influence des rayonnements ionisants sur les complexes antibiotique/récepteur en phase gazeuse
10h00-10h15	C. Alcaraz (LCP, Université Paris Sud) State-selected O2+ reactions with VUV synchrotron radiation for cold plasmas applications
	Pause
	Modératrice : C. Lagrost – Conseil de la DCP
10h45-11h20	**P. Martzel** (Michelin / SimatLab, Clermont Ferrand) **-** ***Conference invitée*** **Simulation multi-échelles de matériaux polymères**
11h20-11h35	A. Pineau (CELIA, Université de Bordeaux) Modélisation de la formation d'un plasma par laser dans le contexte de la fusion par confinement inertiel
11h35-11h50	M. Minisalle (PIIM, Université Aix Marseille) Ammonia production and sticking on materials relevant to fusion reactors: tungsten and 316L stainless steel
11h50-12h05	H. Houjeij (ISM, Université de Bordeaux / IRSN Cadarache) Investigation of CH_3I and CH_3I-H_2O by matrix-isolation FTIR spectroscopy
12h05-12h20	A. Baux (LCTS, Université de Bordeaux) Digitizing gold porous electrodes using FIB-SEM analysis
12h20-12h30	S. Coussan / D. Scuderi Conclusions
12h30-14h00	Déjeuner
	Départ des navettes pour gare et aéroport

CONFERENCE JEAN PERRIN

Hélène Budzinski, (EPOC, Université de Bordeaux),

chimie analytique et chimie de l'environnement

Mieux caractériser les composés "inconnus" dans les mélanges complexes dont les produits de transformation : un enjeu considérable en chimie de l'environnement

CONFERENCES INVITEES

Diffusion Raman et matériaux du nucléaire: imagerie, *in situ* sous irradiation, et résolution temporelle

P. Simon[a], O.A. Maslova[a], A. Canizarès[a], N. Raimboux[a], D. Baux[a], P. Desgardin[a], MF. Barthe[a], F. Duval[ab], R. Mohun[c], L. Desgranges[c], L. Medyk[d], S. Mougnaud[d], PM. Martin[d], M. Tribet[d], S. Peuget[d], C. Jégou[d], N. Galy[e], N. Toulhoat[e], N. Moncoffre[e], F. Garrido[f]

[a] CEMHTI CNRS, Orleans, [b] ISTO CNRS/Univ. Orleans, [c] CEA DEN Cadarache, [d] CEA DEN Marcoule, [e] IP2I CNRS/Univ. Lyon 1, [f] CSNSM CNRS/Univ. Paris Sud

La spectroscopie Raman est utilisée de plus en plus fréquemment pour la caractérisation de matériaux du nucléaire. On présentera ici une revue de résultats récents illustrant les différentes possibilités offertes par la méthode.
En imagerie, sur les céramiques d'oxydes d'uranium, le Raman permet de sonder tout type d'inhomogénéité à l'échelle du µm: différences de comportement coeur-joint de grain, variations de stoechiométrie en oxygène, effets d'irradiation, et éventuelles contraintes mécaniques [1]. La compréhension de ces données sur céramique est facilitée par la connaissance préalable de spectres de monocristaux acquis en fonction de l'orientation.
La possibilité de travailler en mode déporté avec des fibres optiques permet des études *in situ* (matériaux actifs ou irradiations externes par faisceaux d'ions). De telles études en irradiation externe ont pu être appliquées notamment à UO_2 (accès aux cinétiques d'endommagement, à l'échauffement induit par irradiation), sous gaz neutre mais aussi sous eau, où effets d'endommagement du solide et de corrosion radiolytique se cumulent [2]. D'autres études *in situ* ont porté sur des graphites (modèles des modérateurs de centrales UNGG), sous conditions simultanées de pression, de température et d'irradiation ionique. Enfin, le mode Raman déporté permet la caractérisation de matériaux actifs (ATALANTE, CEA Marcoule): combustibles nucléaires usagés [3], ou, récemment, céramiques MOX ($(U,Pu)O_2$) en mode imagerie cette fois.
Enfin, la mesure Raman *in situ* sous irradiation externe est parfois délicate, voire impossible, à cause de la luminescence de l'échantillon (photo- ou iono-luminescence). Des méthodes de résolution temporelle, à l'échelle de la nanoseconde, permettent néanmoins l'acquisition de l'information Raman, avec comme exemple le cas de gels d'altération en surface de verres de stockage.

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Electrocatalyse enzymatique : pourquoi, comment?

V. Hitaishi[a], A. de Poulpiquet[a], I. Mazurenko[a], Elisabeth Lojou[a]

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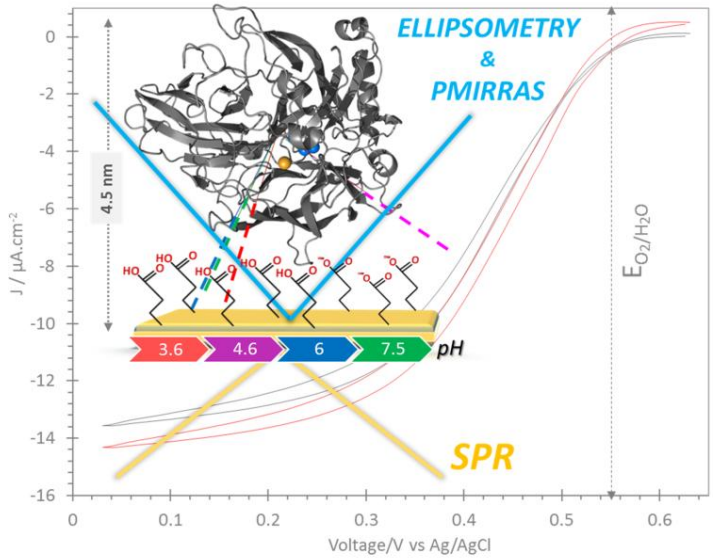
Redox enzymes, that catalyze reactions involving electron transfers in living organisms, are very promising components of biotechnological devices, and can be envisioned for sensing applications as well as for energy conversion [1]. In this context, one of the most significant challenges is to achieve stable and efficient direct electron transfer by tunneling between enzymes and conductive surfaces [2]. Redox enzymes are sizeable proteins with anisotropic properties. Active sites are most often buried inside an insulating protein moiety. Achieving their long term immobilization for efficient catalysis requires specific and controlled orientation at the electrode surface. The fundamental importance of controlling enzyme orientation, how such orientation can be obtained and how it can be verified experimentally are the three main directions that will be discussed in this work. Starting from "in vivo" long distance electron transfer processes inside enzymes and between interacting partners in metabolic chains, we will emphasize the recent understandings we gained through the in-depth study of enzymes for O_2 reduction and H_2 oxidation coming from different microorganisms. Electrochemical interfaces with various surface chemical properties will be considered, with a special focus on self-assembled monolayers on gold and carbon nanotube networks [3]. The ultimate goal is to provide key parameters allowing a rationalization of bioelectrodes.



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Molécules «push-pull » pour le photovoltaïque étudiées par spectroscopie de fluorescence femtoseconde

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Les cellules solaires à colorant (DSSC) ont connu une progression fantastique en termes de rendement et de stabilité depuis leur introduction en 1991 [1]. Leur efficacité de photoconversion dépasse aujourd'hui ordinairement les 10% et un record de 14.3 % a été obtenu [2]. Parmi les diverses axes d'amélioration poursuivis, le développement de nouveaux colorants organiques de type "push-pull" comme photosensibilisateur est particulièrement prometteur. Ces chromophores absorbent en effet plus de lumière du fait d'un spectre large et de haut coefficients d'absorption que les complexes de ruthénium, leur compétiteur comme sensibilisateur. Cependant, au contraire de ces derniers, la dynamique des états photo-induits, en particulier la séparation de charges, est mal connue.
De nombreuses équipes se sont intéressées à ce problème en appliquant diverses méthodes de spectroscopie laser résolues en temps. Il a ainsi été rapporté que l'injection d'électron depuis le colorant photoexcité vers la bande de conduction du semi-conducteur, se déroule sur une échelle de temps très courte (fs à ps).
Ici, nous revisitons certains colorants "push-pull" en solution, sur film et dans des cellules complètes en utilisant la technique de "fluorescence upconversion" [3]. Par une analyse détaillée, nous montrons que le processus d'injection d'électron est un processus complexe s'étendant sur une échelle temporelle très large. Nous montrons aussi que ce processus est fortement inhomogène et implique une compétition entre une relaxation électronique intramoléculaire et une séparation de charges qui dépend de l'état électronique peuplé.

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Femtosecond laser-induced desorption of CO on metals: hot electrons and phonons at play

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Femtosecond laser pulses within the ultraviolet and near-infrared range constitute an efficient tool to promote reactions, diffusion, and desorption of adsorbates at surfaces [1,2]. With laser fluences exceeding 1 mJ/cm^2, reactions start as an indirect mechanism in which the substrate electrons efficiently absorb the laser energy to subsequently release it on the surface lattice and adsorbates. Still, the challenge is to understand the details of these photo-induced surface reactions and identify what factors do actually rule and contribute to initiate the adsorbate dynamics and subsequent reaction: the laser-induced hot electrons, the substrate hot phonons, or the likely interadsorbate energy exchange that may occur at large coverages. In this respect, our ab initio molecular dynamics with electronic friction (AIMDEF) [3-5] method, which has recently been extended to account for the hot electrons and phonons trough time-dependent electronic and lattice temperatures, constitutes a powerful tool to get insight in the nanoscale dynamics of the reaction. Our simulations of photo-induced experiments investigating the desorption of CO from Pd(111) [6] and the desorption and oxidation of CO from Ru(0001) [7] are able to disentangle the role of each of the ingredients involved in such complex scenario.

Acknowledgments: Financial support by the Gobierno Vasco-UPV/EHU project IT246-19, and the Spanish Ministerio de Economía y Competitividad (Grant No. FIS2016-76471-P (AEI/FEDER, UE)).

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Simulation multi-échelles de matériaux polymères

Nicolas Martzel

MICHELIN, SIMATLAB, Clermont Ferrand

Impulsé par une volonté commune de mener une recherche de niveau international sur des problématiques avancées en simulation numérique, le laboratoire SIMATLAB commun à l'UCA et MICHELIN s'est constitué voilà maintenant deux ans.

Nous présenterons le laboratoire, ses principales thématiques ainsi que les travaux de recherche déjà réalisés ou en voie de publication.

La recherche industrielle et académique sont deux mondes qui parfois sont mis en opposition. L'académisme est vu comme détaché des problématiques concrètes, et l'industrie comme faisant peu de cas des thématiques non marchandes.

Ce point de vue oublie l'essentiel de ce qui constitue le terreau de la recherche, les hommes : les physiciens, les chimistes, les numériciens.

PRIX

Prix Jeune Chercheur.e de la SFP

Une goutte, deux vitesses: la dynamique surprenante d'une goutte d'eau sur un élastomère silicone.

Aurélie Hourlier-Fargette[a,b], Arnaud Antkowiak[a], Sébastien Neukirch[a]

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L'utilisation d'élastomères silicones en contact avec des liquides est de plus en plus courante dans de nombreux domaines de recherche, allant de l'élastocapillarité [1] à la microfluidique [2]. Nous nous pencherons sur l'analyse de comportements surprenants observés lors du dévalement de gouttes sur des élastomères silicones, rappelant l'importance de mieux comprendre les phénomènes de mouillage sur ce type de matériaux. La dynamique de descente d'une goutte d'eau sur un élastomère silicone présente deux régimes successifs, caractérisés par deux vitesses différentes. Nous montrons que les chaînes libres non réticulées présentes dans l'élastomère sont à l'origine de cette dynamique inattendue [3]. La goutte est progressivement recouverte par des chaînes de silicone, et sa vitesse change brutalement lorsqu'une concentration surfacique critique est atteinte, ce qui se traduit par une transition brutale de tension de surface. Nous nous intéressons aux vitesses de gouttes dans les deux régimes ainsi qu'aux échelles de temps mises en jeu lors de l'extraction de chaînes non réticulées, et montrons que l'extraction de ces chaînes se produit au niveau de la ligne triple [4].
Cette étude contribue à une meilleure compréhension des interactions entre l'eau et les élastomères silicones et montre qu'une faible quantité de contaminants peut avoir des effets macroscopiques extrêmes.

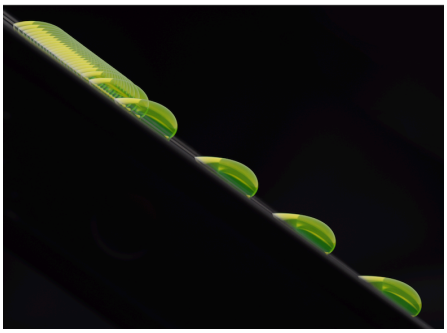

Figure 1 Chronophotographie d'une goutte d'eau dévalant un plan incliné en PDMS (élastomère silicone) : deux régimes de vitesse sont clairement identifiés

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Prix Jeune Chercheur.e de la DCP

The Asymmetry of Life

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What is responsible for the emergence of life's homochiral biopolymers – DNA/RNA and proteins – where all the constituent monomers exhibit the same *handedness*? Based on *in-situ* observations and laboratory studies, we propose that this handedness occurs when chiral biomolecules are synthesized asymmetrically through interaction with circularly polarized light (cpl) in interstellar space.[1] Previous experimental results on the asymmetric photolysis of amino acids,[2] as well as the absolute asymmetric synthesis from achiral interstellar ice precursor molecules,[3] revealed polarization- and energy-controlled induced enantiomeric enrichments.
The recent detection of sugar molecules in interstellar analogue ices[4] (**Fig. 1**) suggests that the molecular building blocks of the genetic material are abundant in interstellar environments and potentially present in comets and small bodies, such as asteroids and interstellar dust particles. I will therefore highlight a few significant results on our on-going cometary ice simulation experiments, the chiroptical properties of targeted sugar molecules in the UV using circularly polarized synchrotron light and present future strategies towards furthering understanding the origin of asymmetric prebiotic molecules.

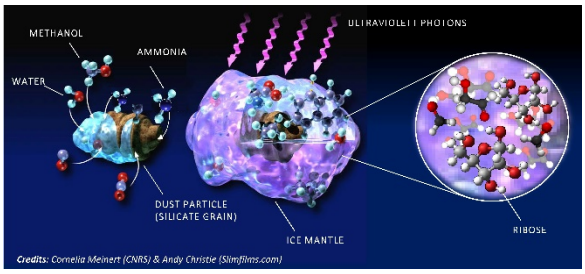

Figure 1 Ribose forms in the icy mantles of interstellar dust grains from simple precursor molecules (water, methanol, and ammonia) under high energy radiation.

ACKNOWLEDGMENTS
Support by the European Research Council under the EU's HORIZON 2020 research & innovation programme [grant agreement 804144] is gratefully acknowledged.

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Prix de thèse de la DCP

Site-occupation embedding theory for the treatment of strongly correlated systems

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Strongly correlated materials (like transition metal oxides) have attracted much attention over the years and remain one of the main central and challenging research topic, gathering chemists and physicists, theoreticians and experimentalists. Being able to understand and even predict the properties of such systems can shape the technologies of the future by the design of new nanodevices, with applications to energy conversion and electronic transport for solar cells, superconducting magnets generating strong magnetic fields, and colossal magnetoresistance materials for magnetic storage.
When it comes to describing strongly correlated materials or molecules, the standard low cost methods such as density functional theory usually fail. While more involved wavefunction-based approaches could in principle be applied, they remain out of reach due to the prohibitive computational cost. A natural and intuitive idea is to merge the two methods to build a new one that gathers all advantages: a low computational cost and good accuracy. From a mathematical point of view, such a combination is very similar to the so-called 'embedding approaches' which are becoming increasingly popular in quantum chemistry[1]. Over the last decade, there has been a clear increase in interest in embedding techniques, which focus only on a small part of a much larger system. One of the most difficult tasks is the incorporation of the nonlocal electron correlation effects induced by the rest of the system (often referred to as the environment). Providing an exact formulation of such a theory is far from trivial since the methods to be merged are written in completely different formalisms.
My thesis dealt with the development and practical implementation of a novel and in-principle-exact embedding approach which is referred to as site-occupation embedding theory (SOET)[2-4]. We first tested it on the Hubbard model, which is mostly used in condensed matter physics for describing strongly correlated materials. Although still in its early stages, promising results have been obtained within SOET and our theory could progress in any of the direction mentioned at the beginning of this abstract.

ACKNOWLEDGMENTS
BS thanks Emmanuel Fromager, Masahisa Tsuchiizu, Matthieu Saubanère, Naoki Nakatani and Vincent Robert for their support and their contributions in this project.

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Prix du chercheur confirmé de la DCP

Un électron peut-il induire un dommage oxydatif à l'ADN? Etude par la radiolyse impulsionnelle picoseconde

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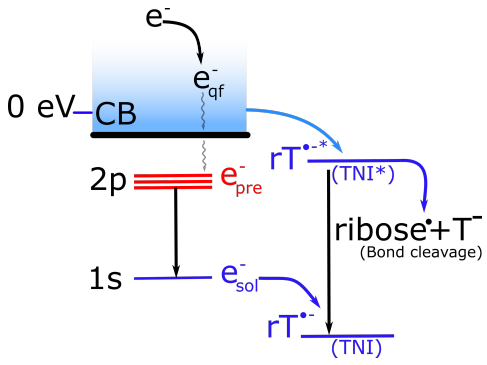
Les dommages causés à l'ADN par l'attachement dissociatif d'électron ont été bien étudiés en phases gazeuse et condensée à très basse température; cependant, la compréhension de ce processus en solution est encore un défi. Dans un environnement aqueux, l'électron non solvaté et solvaté sont des systèmes plus réalistes d'électrons en biologie que ceux en phase gazeuse. L'étude de la réduction ultra-rapide de modèles simples de biomolécules (p. ex. nucléobases et nucléosides/tides) par un électron en solution en compétition avec son processus d'hydratation est un sujet de débat.

Nous avons utilisé les impulsions picoseconde d'un faisceau d'électrons à haute énergie de la plateforme ELYSE pour générer des électrons dans le diéthylène glycol liquide (solvant polaire dans le quel ribothymidine est très soluble) et pour observer la dynamique de fixation des électrons secondaires à la ribothymidine lors leur étapes de relaxation. Nos résultats en spectroscopiques pompe (faisceau d'électron)-sonde (faisceau de laser) révèlent que l'électron quasi libre se fixe efficacement à la ribothymidine, ce qui mène à la formation d'une nouvelle espèce absorbante qui a été bien caractérisée dans la région visible aux UV juste après l'impulsion d'électrons de 5 ps. Cette espèce présente une dissociation indépendante de sa concentration avec une constante de temps de ~350 ps. En performant des measures dans différentes conditions et en analysant les données de manière rigoureuses, nous avons assigné cet intermédiaire à un radical anionique excité qui subit une dissociation de liaison glycosidique N1-C1′ plutôt que la relaxation à son état fondamental. Ainsi pour la première fois, nos mesures montrent qu'en solution un électron non solvaté peut induire un dommage comme celui induit par la voie oxidative à l'ADN.



Différents états des électrons dans le processus de relaxation et de solvatation dans un milieu polaire après passage d'un rayonnement ionisant en présence de ribothymidine (rT). Electron en excès dans la bande de conduction (CB) représentant un électron quasi libre (e_{qf}^-), qui finit par être piégé (e_{sol}^-) dans la cage du solvant. Les électrons capturés par les molécules du soluté produisent des anions transitoires ($rT^{\bullet -}$). A l'état excité, l'anion peut soit libérer l'énergie excédentaire, soit subir une rupture de liaison (dissociation).

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Prix d'Instrumentation

SpectroElectroChimie d'Absorption (A-SEC) en temps réel : De la molécule à la monocouche.

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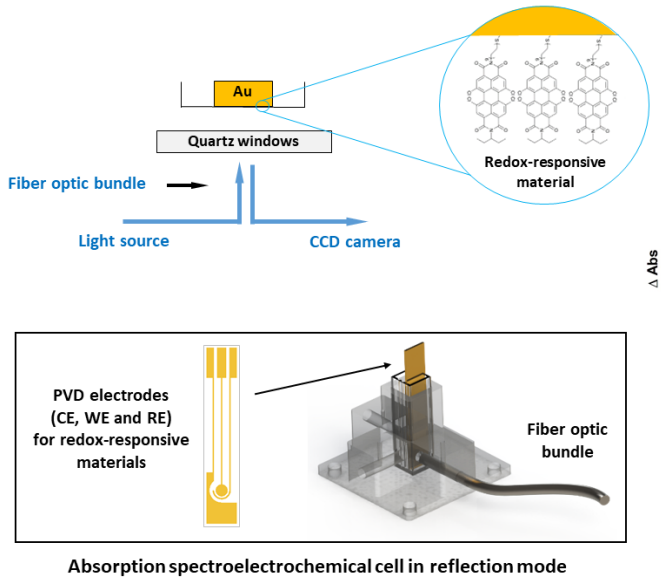
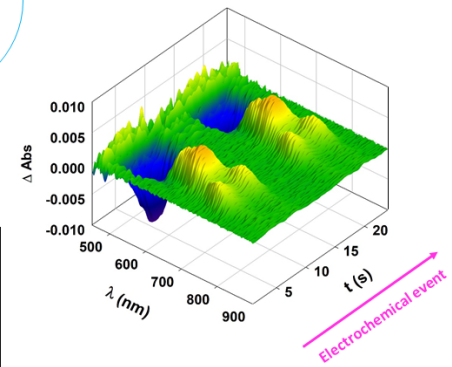
La course effrénée vers les nanotechnologies a conduit au développement d'électrodes modifiées de plus en plus petites en épaisseur ; l'état ultime étant la monocouche auto-assemblée (SAM).
Dans le domaine de l'électrochimie, la dimensionnalité nanométrique n'a jamais été un problème car le facteur limitant n'est pas l'épaisseur de la couche, mais la surface de l'électrode. Cependant, l'échelle nanométrique de la couche électroactive limite la possibilité de caractériser la SAM par des méthodes spectroscopiques d'absorption et d'émission "standard".



Absorption spectroelectrochemical cell in reflection mode



Spectroelectrochemical response

Nous allons présenter ici un banc de mesures spectroélectrochimiques capable d'identifier des signatures optiques de très faibles intensités dans le domaine du visible-NIR et illustrer les potentialités de ce banc via des exemples dédiés principalement aux SAMs.[1-5]

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RESUMES DES COMMUNICATIONS ORALES

Approche multi techniques pour la caractérisation de carbènes élusifs

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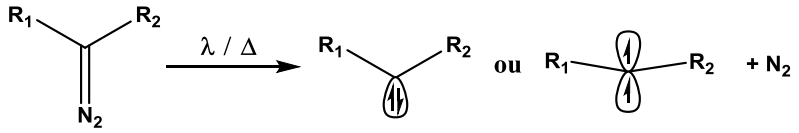
L'observation directe des intermédiaires réactionnels est rare en raison de leur durée de vie intrinsèquement faible. Toutefois, les informations que l'on peut en déduire (propriétés structurales et électroniques) sont cruciales et très utiles pour la compréhension des mécanismes réactionnels des processus chimiques dans lesquels ils sont impliqués. La caractérisation d'espèces transitoires nécessite des méthodes spécifiques et des conditions expérimentales adaptées. Nous possédons au laboratoire deux techniques analytiques particulières qui permettent leurs identifications, à savoir la spectroscopie photoélectronique à rayonnement UV en phase gazeuse (SPE-UV) et le piégeage cryogénique couplé à la spectroscopie infrarouge (IR). Les espèces élusives sont quant à elles synthétisées en amont grâce à des réactions de photolyse ou de thermolyse de précurseurs adaptés.

Nous avons utilisé cette approche originale afin de caractériser des carbènes dont la courte durée de vie n'a pas permis, jusqu'à aujourd'hui, leur identification directe. Ces carbènes sont générés par réactions de photolyse et/ou thermolyse de précurseurs diazoïques :



R_1 : $SiMe_3$
R_2 : H, $SiMe_3$, CH_2SiMe_3

Notons que H. Shester [2], T. J. Barton [3], et W. Sander [4] ont précédemment postulé le passage par de tels carbènes mais les travaux réalisés n'ont permis de caractériser que des composés de réarrangement thermodynamiquement stables.

Ainsi, les différents intermédiaires ont été caractérisés *in situ* par leurs potentiels d'ionisation en phase gazeuse grâce à la SPE-UV ainsi que par spectroscopie IR après piégeage sur matrice d'argon à quelques K. L'attribution des ionisations sur les spectres photoélectroniques a été réalisée grâce à des calculs DFT (position et nature des orbitales moléculaires). La modélisation a également permis de proposer les mécanismes de décomposition mis en jeu.

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Innovative Atrazine microfluidic colorimetric sensor based on barbiturate derivatives microcrystals

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The detection of polluting species in the environment (water, soil, air, food, manufactured products) is a major public health and environmental issue. Nowadays, many substances are classified as probable carcinogens, reprotoxic or mutagenic, while their utilization remains highly developed. This is particularly the case for certain herbicides/pesticides used in the agri-food industry such as glyphosate, atrazine or dicamba. The presence of residues in finished products, soils or water is strictly regulated by environmental standards, which tend to be more and more restrictive. However, if control standards are required, the available analytical techniques must match. This involves the development of analytical techniques that both address the issues of sensitivity, reliability and cost.

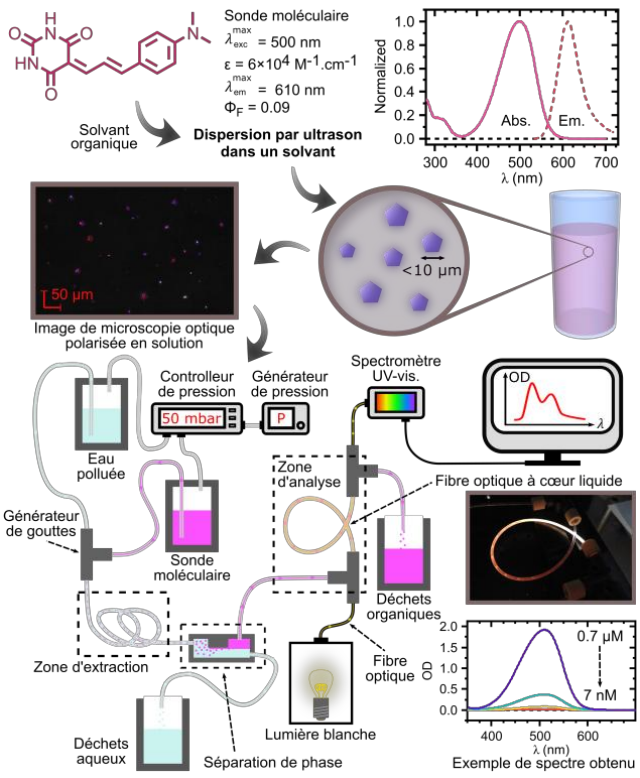

Figure 1 : Illustration of the detection setup

Among all the compounds available, Atrazine has been extensively employed in the intensive agri-food industry as herbicides over the past five decades. Despite its banning in the European Union since 2003 it is still in use in numerous countries around the world and it is widely present in the environment due to its remarkable retention in soil and poor solubility in water. This compound as well as its degradation products are highly toxic, potentially endocrine disruptor and carcinogenic.[1]

Therefore, in order to achieve efficient Atrazine detection and meet the regulation standards, numerous methods have already been reported.[2] Here we present another approach using a microfluidic detection sensor based on phase extraction from water to organic solvent combined with colorimetric molecular recognition by micro-crystalline barbiturate derivatives (**Fig. 1**).[3]

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Research of Interactions in U(IV)/U(VI) Mixtures

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[b] *ICSM, LMCT*

This work focused on the simplicity of the uranium (IV) and uranium (VI) mixtures through different means such as water activity or density measurements using the simple solution approach [1, 2].

Since these two elements are mixed together in the PUREX process during the partition step, which separates the uranium from the plutonium, the knowledge of the behaviour of this mixture will help the modelling of this process. This will allow a more precise code to be developed and thus a better modelling of the different components involved in the PUREX process.

Lately, thermodynamic codes are developed taking into account deviation from ideality. Thus the behaviour of each system has to be known. In other words, all the interaction between 2 molecules have to be quantified.

In order to check whether the mixture is simple or not, the simple solution approach has been chosen because of the simplification made to the acquisition of the data. The simplicity of the uranium (IV) uranium (VI) mixture will be checked using different methods and an analysis of these methods will be made to verify the validity of the results. This will be made through the acquisition of water activity, density and molality from different solution of uranium (IV) and uranium (VI).

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Multi-wavelength Raman microscopy: investigating physico-chemistry on tokamaks walls

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Due to plasma surface interactions (PSI), many processes will modify the plasma facing components (PFC) of magnetically confined fusion reactors like ITER, which are designed to study the possibilty to make energy exploiting the nuclear D+T reactionMetallic PFC (C in the past years, mainly Be and W nowadays) can be modified during their lifetime (melting, deposition, erosion, creation of defects, amorphization, formation of: reactive dusts, oxides, hydrides, hydroxydes...). However, one of the major concerns from a safety issue point of view is about T retention in the walls, as T is radioactive. Predicting how much T will be trapped is then mandatory. This work is done mainly in the framework of the EUROFUSION consortium [1]. Here, we will focus specifically on the use of Raman microscopy that gives information on the way hydrogen isotopes and other elements are bonded together. We will then give concrete examples on how Raman microscopy can be used to characterize, with a spatial micrometric resolution, both samples synthetised in laboratory to mimic samples coming from tokamaks (defective Be, Be_xC_y, BeD_2, $WO_{3-x,}$...[2,3]) and samples directly extracted from tokamaks (presence of $Be_xO_yD_z$ in melting region of tokamaks [4]). The use of several laser wavelength when doing Raman spectroscopy allows to probe few tens of nanometer down to the surface. This point will also be adressed.

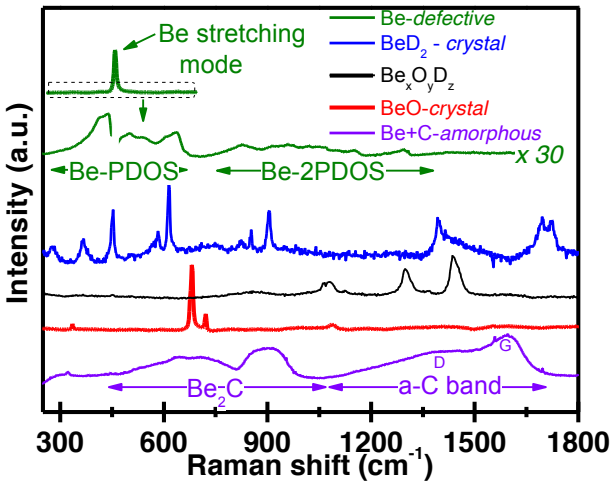

Figure 1 Raman spectra of Be based samples.
PDOS refers to the phonon density of states of Be

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New sodo-niobate amorphous thin films: microscale patterning of strong second order optical response by thermal poling)

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Amorphous materials presenting high second order (SO) optical response are of great interest to design active optical devices. In this study, we report on a thermo-electrical treatment used as an imprinting process that breaks the natural centro-symmetry of an amorphous material and induce SO optical response. The synthesis of new sodo-niobate amorphous thin films has been achieved by RF sputtering in a range of composition spanning from pure Nb_2O_5 up to 10 at.% of sodium. The effects of the thermo-electrical imprinting process are characterized using a correlated Raman/Second Harmonic Generation microscopy technique allowing correlations between structural changes and nonlinear optical properties at the micrometer scale. The induced SO optical response is quantified and the probed anisotropy is controlled by tuning the incident beam between linear, radial and azimuthal polarization state. The SO susceptibility ($\chi^{(2)}_{zzz}$) is found to worth 6 pm/V in a homogeneously polarized zone of the film and 37 pm/V close to the edge of the electrode. This is the highest value ever reported in non-crystalline heavy oxide materials.

X-RAY RESILIENT SILVER-BASED STRUCTURES GENERATED BY INFRA-RED FEMTOSECOND LASER: UNDERSTANDING OF THEIR ORIGIN AND FORMATION MECHANISM

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In the two last decades, Direct Laser Writing (DLW) using infra-red femtosecond (IR fs) laser has been carried out to perform glass network photo-structuration leading to multiple applications. In the specific case of silver-containing phosphate glass, DLW by extrinsic photo-structuring leads to the local formation of silver clusters, giving rise to remarkable optical properties such as photoluminescence, 2nd- and 3rd-harmonic generation, development of silver plasmonic nano-particles and demonstration of a novel type of silver-sustained single-mode waveguides. The control of the fs laser energy deposition and the glass composition has allowed for demonstrating two fluorescent sub-micron lines inscription regimes.

Various Oxygen-to-Phosphorus ratio glasses have been investigated by spectroscopy measurements (Raman, photoluminescence, absorption, etc.) to determine both the glass structure and the silver ion environment. Meanwhile, the mechanisms of the silver cluster formation have been also studied by conducting linear absorption irradiations under UV nanosecond laser or X-rays sources. Such irradiations lead to non-luminescent and luminescent silver-based species, which have been identified and tracked by absorption, steady state and time resolved fluorescence spectroscopy as well as electron paramagnetic resonance. Finally, the fiber drawing of selected silver-containing phosphate glasses has been demonstrated, emphasizing the potential of these materials for developing new photosensitive fiber devices.

Metallic Nanoparticles Functionalized with Calix[4]arenes as Selective Catalysts for Oxygen Reduction Reaction (ORR)

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In the race of new technologies keen to obtain new sources of low-cost and sustainable energy, activation of abundant small fuel molecules (such as O_2, H_2O, CO_2 and H_2) is now widely studied to convert their chemical energy into an electric one[1]. However, the multi-electronic processes commanding these activations are not yet fully understood and controlled, but they have been observed to be efficiently catalyzed in nature through the action of metalloenzymes, in which a catalytic site is buried inside a organized molecular environment reguling the reactivity.

The strategy presented here, directly inspired from metalloenzymes, to control the interfacial reactivity at the molecular level is based on the functionalization of metallic nanoparticles by a monolayer of calix[4]arenes(ref) that will behave as nanocavities. It is believed it will influence the orientation and approach of the O_2, but also the nature and lifetime of intermediate species produced during electrocatalysis through supramolecular interactions.

Herein, we will present the electrochemical properties of these systems with the prospect of obtaining efficient and mostly highly selective catalytic system for the ORR.

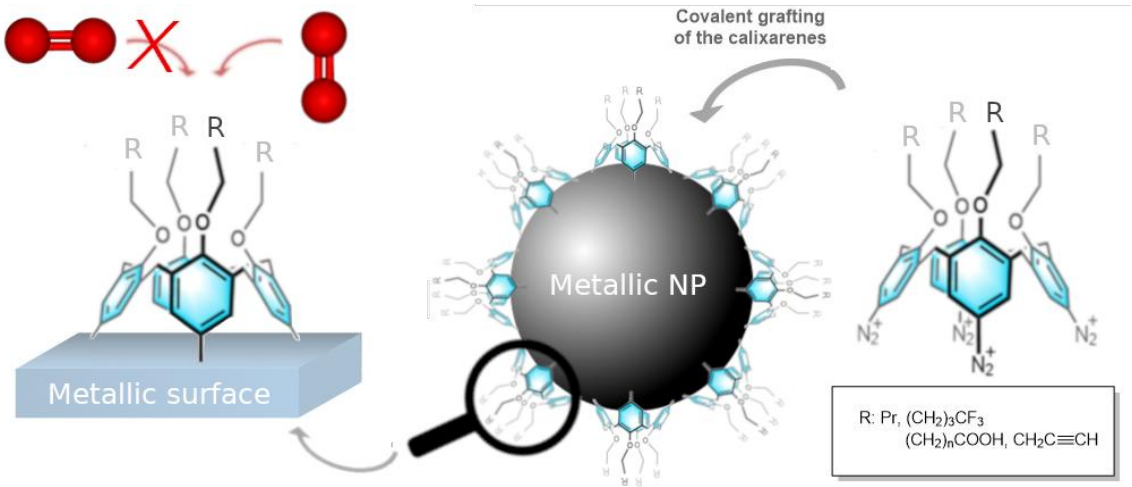

Figure 1 Grafting of calix[4]arenes on metallic NPs and its influence on O_2 adsorption mechanism

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Photo-Induced Electrochemiluminescence by Upconversion at Silicon Electrodes in Water

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Electrochemiluminescence (ECL) is a light-emitting process and a powerful tool in analytical chemistry. This phenomenon is induced by the excited state of a luminophore, which is generated by an electrochemical reaction at an electrode surface.[1] Conversely, photoelectrochemistry on illuminated semiconductors (SCs) is a process where an electrode absorbs light, and that can be used in order to decrease the potential required to trigger an electrochemical reaction.[2]

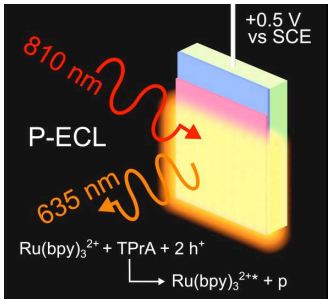

Figure 1 Scheme showing the P-ECL phenomenon.[4]

In this communication, we introduce the photo-induced electrochemiluminescence (P-ECL, Figure 1) of the model anodic ECL system involving $[Ru(bpy)_3]^{2+}$ and tri-*n*-propylamine (TPrA). In the reported approach, the ECL emission is triggered by holes photogenerated in an *n*-type semiconductor (SC) electrode, which is normally highly challenging due to competing photocorrosion occurring at SC electrodes in aqueous electrolytes.[3] We employ here Si-based tunnel electrodes protected by a few nm-thick SiO_x and Ni stabilizing thin films and demonstrate that this construct allows generating P-ECL in water. This system is based on an upconversion process where light absorption at 810 nm induces ECL emission (635 nm) at a record low electrochemical potential of 0.5 V *vs* SCE. Neither this light excitation nor this applied potential is able to stimulate ECL light when applied separately, but their synergetic actions lead to a stable and intense ECL emission in water.[4]

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Optical fibers for Confocal Microscopy under Electrochemical control: A case study with electrofluorogenic species

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Biosensors are powerful analytical tools that enable the detection of targeted biomolecules, particularly for clinical diagnosis or food traceability. In that context, electrochemical biosensors offer good transduction capability thanks to the ease of implementation, low cost of measurement and facility of integration.[1] Conventional electrochemical measurement can be carried out with either macroscopic or microscopic electrodes and allow to probe electrochemical reactivity of species. Those kind of measurements are time-resolved but the electrochemical response is averaged over the entire electrode area preventing access to local surface heterogeneity. To address this problem, we propose to develop a coupled measurement technique allowing to record images of the surface by confocal fluorescence microscopy under electrochemical control.[2] Coupling electrochemistry with confocal fluorescence microscopy allows to obtain 3-dimensionnal spatial information and provides a fine evaluation of the homogeneity of the surface with good temporal and spatial resolutions thanks to the confocal mode. In order to achieve such *in situ* coupling, the first step consists in the preparation of tunable optoelectrodes based on optical fiber array that will be suitable for simultaneous optical and electrochemical measurements.[3] Optical fibers just as microelectrodes are widely used in bioanalysis or as chemical sensors.[4] With their good spatial resolution, they enable to probe concentration profiles of relevant chemical species at micro-/nanoscale. The present work focuses on a biorelevant electrofluorogenic phenoxazines such as resazurin whose fluorescence properties is modulated by its redox state. This proof-of-principle will demonstrate the experimental possibilities to visualize the diffusion layer of a (micro-) electrode using a confocal microscope.

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Halogen Bond and Electrochemistry: A promising cooperation for controlling supramolecular architectures in solution and on surface

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Halogen bonding (XB) has recently gained increasing interest in the scientific community. XB are non-covalent interactions and occur when there is a net attractive interaction between the electrophilic region (σ-hole) of a halogen atom (XB Donor) and a nucleophilic region in another, or the same, molecular entity (XB acceptor). Few examples have been described in solution until now, but they have already clearly highlighted the importance of XB interactions in molecular recognition, anion sensing and transport, medicinal chemistry and catalysis [1].
Concerning activation and detection of XB in solution, electrochemical techniques remain almost absent in the literature (see our recent work [2-4]). In this communication I will present all the potentialities of electro-stimulating XB for molecular recognition of relevant anions, neutral Lewis bases and halo-perfluorocarbons *via* a reversible electrochemical reaction.
The use of redox active XB donors to switch ON/OFF XB interactions is very attractive and will give access to unprecedented properties.
Exploration and generalization of this concept as well as its application for analytical purposes is an original and highly innovating task.
Moreover, I will also focus on the transfer of this concept onto an electrode surface. Interfacial XB will be proven using electrochemical techniques such as cyclic (CV) and square wave voltammetry (SWV).

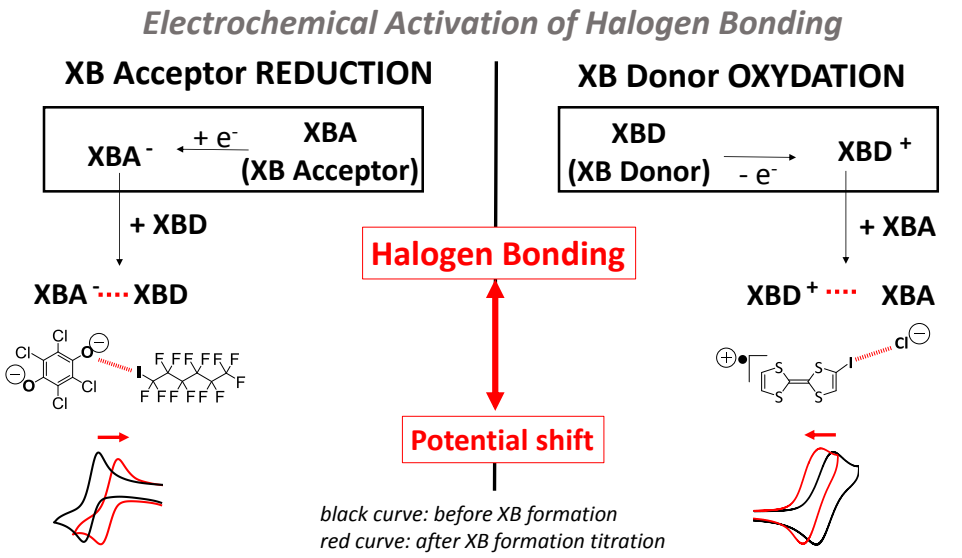

Figure 1: Electrochemical Activation of XB via reversible redox switching

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Electronic properties of heterobimetallic complexes of lanthanide and transition metal

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Transition metals are widely used from coordination study towards reactivity and catalysis. From C-H activation of alkanes [1] to CO based reactivity [2], they are one of our main hopes to achieve greenhouse gas valorization.

In our group we are focused on heterobimetallic complexes combining a divalent lanthanide fragment, a redox active ligand (RAL) and a transition metal.

In those complexes, the divalent lanthanide is a multiconfigurational supplier of one electron [3]. The RAL's ability to accept an electron that interacts with the transition metal fragment [4, 5] allows a modulation of the valence electronic structure that influences the reactivity on the transition metal [5, 6]. Continuing our work with group 10 (Pd and Ni), we now present the spectroscopic and computational studies on the [Yb^{III}(bipym)Pt^{II}] and [Yb^{III}(bipym)Pt^{IV}] complexes. Finally, we introduce our work on group 9 transition metals, with a novel [Yb^{III}(bipym)Ir^{I}]$^{+}$ cation.

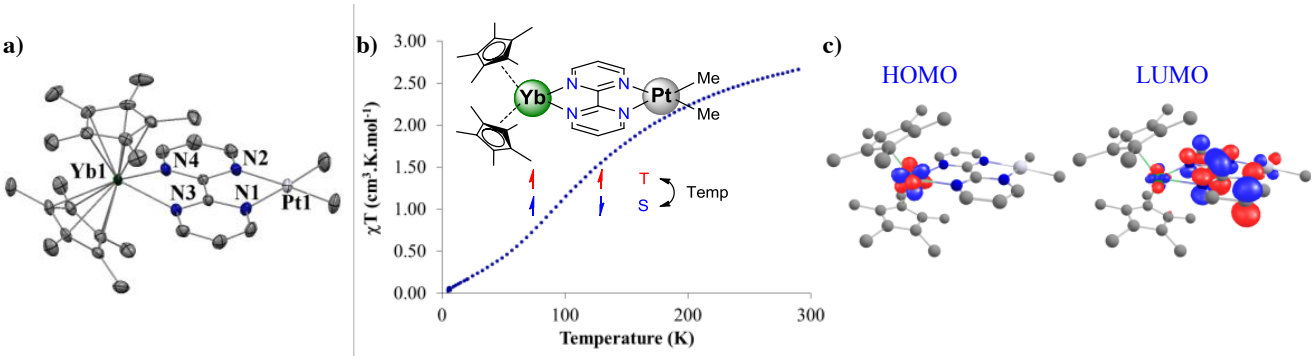

Figure 1 : Overview of the study for [Yb^{III}(bipym)Pt^{II}], **a)** ORTEP of the complex, **b)** Magnetic study, **c)** Kohn-Sham orbitals from PBE DFT study for the singlet state.

ACKNOWLEDGMENTS

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Propriétés vibrationnelles de nanoparticules auto-organisées de cobalt et de coeur/coquille cobalt/oxyde de cobalt

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Les propriétés physico-chimiques des nanoparticules diffèrent de celles des matériaux massifs. Nous avons synthétisé des particules de cobalt de taille contrôlée[1]. Elles peuvent sous certaines conditions s'organiser en "supercristaux" de taille micrométrique. Nous avons utilisé les spectroscopies vibrationnelles infrarouge et Raman pour étudier ces objets et comprendre les interactions entre l'agent passivant et le métal. Nous avons également obtenu la signature Raman dans le domaine des bas nombre d'ondes, qui est interprétée selon le modèle de Lamb[2].
Dans un deuxième temps nous avons partiellement oxidé ces nanoparticules pour synthètiser des systèmes "coeur/coquille" dont nous présenterons les propriétés vibrationnelles.

ACKNOWLEDGMENTS

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Chemical Tuning of Coulomb Blockade at Room-Temperature in Ultra-Small Platinum Nanoparticle Self-Assemblies

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Even if Coulomb blockade has been studied for over sixty years, and previously observed at room temperature, the new concept of our work is its fine modulation, which can be achieved by a controlled organometallic chemistry approach, as a first step toward electronic devices. The goal is to tune Coulomb blockade in dense three-dimension self-assemblies of metallic nanoparticle with simple chemical tools. Synthesizing robust systems – stable in air for months – is a crucial condition; platinum nanoparticles stabilized by thiols, which form strong Pt-S bonds, are suitable systems. This presentation will describe a system where the nanoparticle size, the ligand length and the ligand dielectric constant are independently varied to control the nanoparticle charging energy. Such a chemical approach allowed the determination of the most important parameters that influence Coulomb blockade, namely the dielectric constant of the ligands and the size of the nanoparticles. Elaborating such systems, stable in air for months, is a first step towards nanoelectronic systems, where the charging energy of the nanoparticles is tuned by the nature of the ligands.

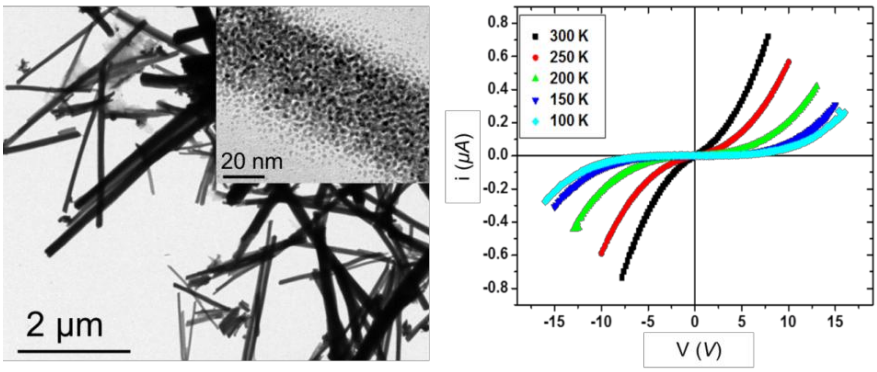

Figure 1 Platinum nano-particle assemblies in the presence of mercaptophenol: *left*: regular and zoomed (inset) TEM picture; *right*: charge transport measurements at temperatures ranging from 100 K to 300 K.

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Intracellular Biotransformation of Gold Nanoparticles

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Gold nanoparticles (GNPs) are used in an expanding spectrum of biomedical diagnostic and therapeutic applications[1] while little is known about their fate at long term in the organism. The current dogma is that the inertness of gold prevents biodegradation of gold nanoparticles.
We describe the biotransformations of gold nanoparticles in primary human fibroblasts during 6 months. We reveal the intracellular degradation of gold nanoparticles with a size dependent kinetic and the apparition of specific degradation products, constituted of 2.5 nm crystalline particles self-assembled into nanoleaves. We demonstrate that these degradation products are similar to structures revealed fifty years ago *in vivo* after gold salt injection. This support the original idea that the fate at long term of ionic gold and of crystallized GNPs is the same. Transcriptomics analysis reveals long term oxidative response to GNPs involving NFE2 pathway and MTs production. On this basis we propose a potential mechanism of GNPs biotransformation compatible with transcriptomic analysis and which appears experimentally credible in the light of our results. Our work provides first an in vitro methodology to study persistent nanoparticles on the long term that is consistent with in vivo studies, and enables a deeper understanding of gold nanoparticles metabolism.

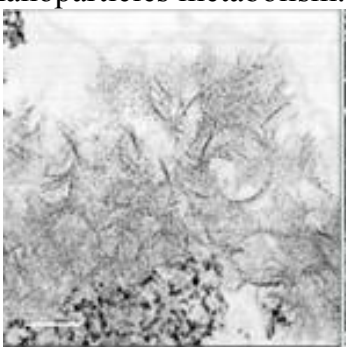

Figure 1 STEM observation on microtome section of human fibroblasts two weeks after exposure to 4 nm GNPs showing that degradation products are 2D nanoleaves composed of self-assembled 2.5 nm nanoparticles. Non degraded NPs can be seen at the bottom of the image.

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Mechanofluorochromic properties of an AIEE-active 2-phenylbenzoxazole derivative: more than meets the eye?

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Stimuli-responsive organic materials that exhibit fluorescence emission changes upon mechanical stress in the absence of any chemical reaction, i.e. mechanofluorochromic (MFC) materials, are in great demand for applications as polymer stress sensors, security inks, data storage and memory devices [1,3]. We looked for this property in the 2-phenylbenzoxazole (PBO) series, many derivatives of which are known for their excellent stability and unique emission properties in the solid state [4]. The presence of a dicyanovinyl group on the robust 2-PBO framework (Compound **1**, Fig. 1) led to the emergence of aggregation-induced emission enhancement (AIEE) and MFC behaviour. The pristine microcrystals emitted yellow-green light, which became golden yellow upon grinding, and *vice versa* by heating or solvent fuming. This phenomenon was accompanied by a reversible evolution of the photoluminescence quantum yields and lifetimes. These variations were attributed to the formation of different types of emissive species in the crystalline phases and in the ground, partly amorphous material. Evidence was also given for other spectroscopic effects, such as light reabsorption, which depend on the size, compactness and heterogeneity of the solid samples. Confusion between these effects and the genuine MFC effect could explain the apparent lack of repeatability and reproducibility that may be encountered in this delicate field of research [5].

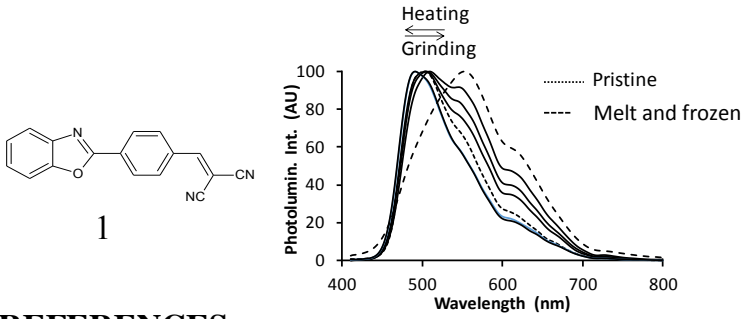

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Figure 1. Photoluminescence spectra of the various solid samples: pristine micro-crystalline powder; powder afte heating and grinding; polycrystalline melt and frozen sample (λ_{ex} = 380 nm).

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Photochromic molecules and plasmonic materials for new reversible switchable devices

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Using metallic nanoparticles (NPs) for electronic devices show many advantages due to their specific optical and electric properties that can be driven by light. In fact, surface plasmon resonance is very sensitive to their direct environment, it is possible to use photochromic molecules as a local photoswitch to reversibly modify these photophysical properties. [1] The goal is to develop a hybrid material combining molecular and plasmonic components which by action of an external stimulus – here a light excitation - shows a reversible change of its electrical - conductance - and optical properties at the millimeter scale. [2,3]

In this communication we present hybrid nanomaterials made of (i) gold nanorods as the plasmonic unit [4] and (ii) charged diarylethene as photochromic unit. A polyelectrolyte is used as a linker between them thanks to electrostatic interactions, limiting the quenching of the photochromic molecules. Steady state absorption experiments highlight the fact that using polyelectrolyte as linker avoids the quenching of the photochromic reactions. Furthermore, transient absorption experiments clearly show that the hybrid nanomaterial behaves differently from the single gold nanorod or diarylethene.

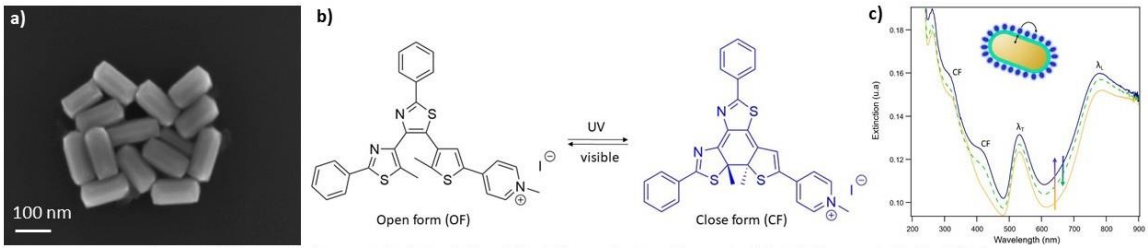

Figure 1 a. SEM image of gold nanorods, **b.** photoswitching of diarylethene and **c.** absorption spectra of the hybrid nanomaterial after irridiations (370 nm to go from OF to CF, 543 nm to go to CF to OF)

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Hybrid nanostructured thin films, optically tunable.

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Nowadays, micro- and nanopatterning of surfaces, thin films or multilayer structures *via* lithography-based technologies are widely used to design optical devices. However, they are based on complex processes and suffer from several drawbacks in terms of cost, material compatibility and device tunability. Recently, alternative approaches are proposed which exploit the properties of azobenzene-containing photoactive soft materials [1,2]. These materials are compatible with simple low-cost deposition and patterning processes and their mechanical response to light excitation allows one to envisage devices with tunable properties that can be controlled by a contactless optical stimulus [3].

We will present simple routes to elaborate micro- and nanopatterned metal / dielectric structures that exploit the photo-mechanical response of azobenzene-containing materials for controlling the shape of the structure pattern at the microscopic scale by illumination in the chromophore absorption band. The optical properties of the device are shown to exhibit spectacular changes related to the photo-induced modifications of the pattern shape (Figure 1).

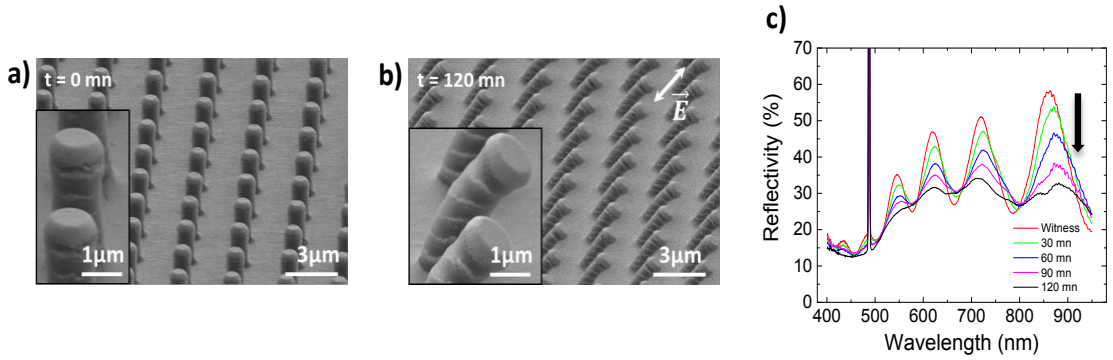

Figure 1 PMMA-DR1/gold micro-pillar array obtained by a combination of soft micromolding and metal evaporation, before (a) and after (b) 120 mins of illumination with 25 mW/cm^2 of p-polarized light in the absorption band of the azobenzene derivative (488nm). c) Evolution of the optical reflexion spectrum of the structure as a function of illumination time.

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Multi-scale investigation of mechanofluorochromism of a donor-acceptor compound

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Molecular solids that respond to mechanical stimuli by a change in photophysical properties have attracted attention in recent years due to applications such as optical storage devices, security papers, and force sensors.[1] Such technologies are varied not only in terms of the types of devices but the different scales at which such devices may be fabricated and applied as well. In this context, we present a multi-scale investigation on the mechanofluorochromic behavior of a donor-acceptor compound (Fig1a). In the macroscale, thin films of the compound showed evolution of fluorescence properties over time and upon mechanical stimulation (Fig1b). Optical microscopy revealed two polymorphs present on the films: thread-like nanostructures and microcrystals. Atomic force microscope (AFM) and confocal microscope probed the topography and fluorescence properties of both polymorphs. Fluorescence increase concomitant with topography changes were observed upon mechanical stimulation by contact-mode AFM. (Fig 1c,d) Fluorescence spectra collected for these respective polymorphs could be correlated with the spectra measured in the macroscale.[2] This study opens up this compound for applications to smart self-healing materials and force sensors not only in the macroscale but in the micro/nanoscale as well.

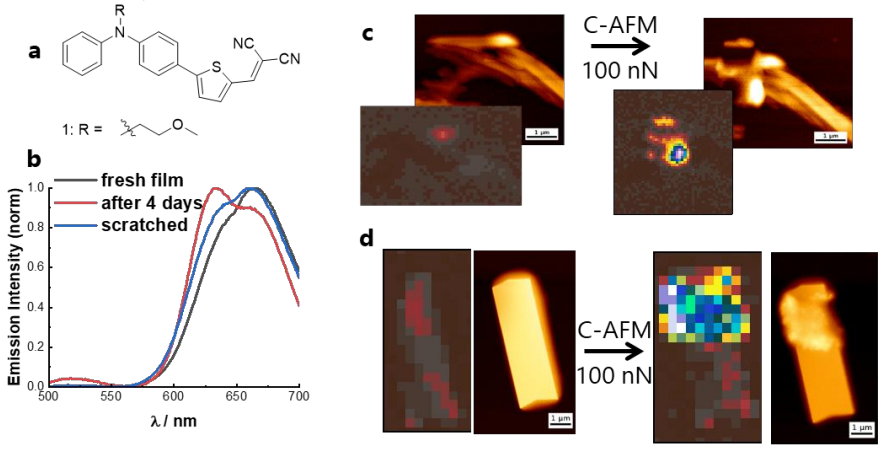

Figure 1. a) Structure of compound. b) Changes in the fluorescence spectra of the thin films. (λ_{ex} = 480 nm). (c-d) Confocal and AFM topography images of the nanofibers (c) and microcrystals (d) before and after contact-mode AFM show increase of fluorescence coupled by a change in topography.

ACKNOWLEDGMENTS

This work was made possible through the ERC StG-715757 MECHANO-FLUO grant.

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Matériaux mécanofluorochromes : quantification de leur réponse à des stimuli mécaniques

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Un composé dont la fluorescence à l'état solide est modifiée suite à l'application d'une force mécanique externe est dit mécanofluorochrome [1]. L'incorporation de tels composés dans des matrices polymères hôtes confère au matériau composite résultant un comportement mécanofluorochrome [2]. La possibilité de suivre ce changement de fluorescence à distance, par des mesures spectroscopiques non invasives en fait de bons candidats pour des sondes de contraintes mécaniques.

Les complexes de bore dicétone (comme le DFB-H) et les dérivés de triphénylamine (comme TPA1) sont connus pour leur mécanofluorochromisme à l'état de poudre (Figure 1a). Cependant, à notre connaissance, il n'existe pas d'expériences quantitatives permettant de remonter à la force appliquée sur ces poudres à partir du changement de fluorescence observé. De plus, des expériences de broyage en mortier ne permettent pas de trancher sur les types de contraintes (compression, cisaillement) auxquelles ces poudres sont sensibles.

Lors de cette communication, un montage permettant d'appliquer une compression et un cisaillement sur un matériau mécanofluorochrome sous irradiation sera présenté. Grace à ce montage il est également possible d'enregistrer des images de la fluorescence de l'échantillon pendant la contrainte mécanique et de relever les valeurs de force et de couple. Une procédure de traitement de ces données a été développée afin de quantifier le cisaillement seuil nécessaire pour observer le mécanofluorochromisme du DFB-H et du TPA1.

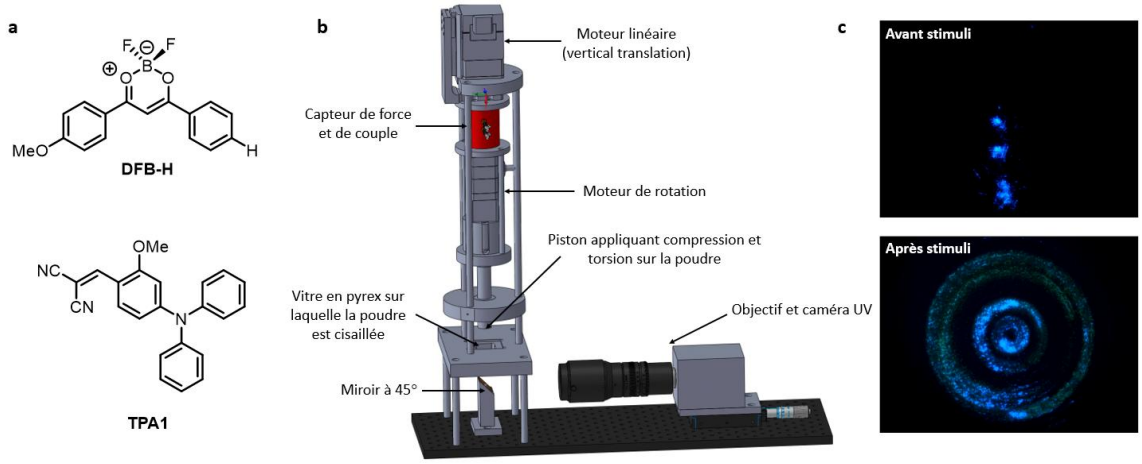

Figure 1 (a) Structures du DFB-H et du TPA1, (b) schéma du montage pour la quantification de la réponse mécanofluorochrome et (c) images d'expériences réalisées avec ce montage sur une poudre de DFB-H.

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Photopolymerization at the nanoscale controlled by plasmon resonance

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Over the past ten years, localized surface plasmons have been exploited for triggering and controlling photochemical and photophysical reactions. Achieving hybrid nanosystems coupling metal nanostructures with enhanced effect is a major challenge for applications in nanophotonics, sensors or spectroscopy.
In our case, surface plasmon resonance of individual metal nanoparticles was used as an optical near-field source to locally trigger free radical polymerization of an acrylic monomer: metal nanoparticles embedded in a photopolymer sensitive at the resonance wavelength are irradiated under the polymerization threshold but close enough to this threshold to initiate the free-radical polymerization thanks to electromagnetic near-field enhancement.
We will report on the physicochemical and optical parameters controlling the photopolymerization process in near-field. Kinetic parameters were shown to be of paramount importance to control the polymerization in highly confined space. Different photopolymers were used in this context to finely tune the final properties of the nanoparticles.

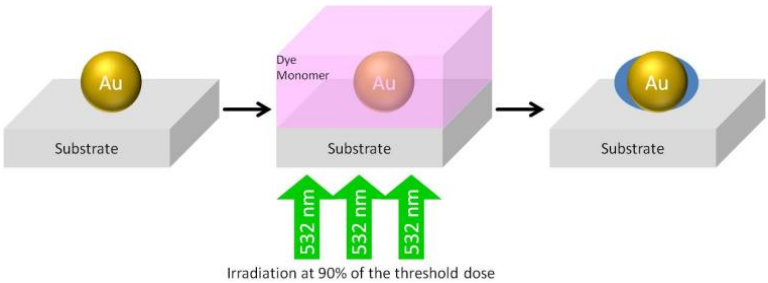

Figure 1. Experimental principle of the photopolymerization on the near-field of gold nanoparticles.

ACKNOWLEDGMENTS

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Stochastic energy shuttling in molecular machines and supramolecular systems

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Interchromophore Reversible Electronic Energy Transfer (REET) may be instilled in bi-/multichromophoric molecule-based systems, following photoexcitation, upon judicious structural integration of matched chromophores.[1] This leads to a new set of photophysical properties for the ensemble, which can be fully characterized by steady-state and time-resolved spectroscopic methods.[2,3] Combining transition metal complexes with matched organic chromophores has proven a reliable strategy to instil this process, taking into account specific kinetic and energetic considerations. Herein[4,5], we show prototype synthetic molecular machines, exemplified by different molecular ring-on-thread rotaxane structures, exhibiting REET. Indeed, this process holds promise in the control of movement in molecular machines or assembly / disassembly as well as photosensitizers for charge separation.

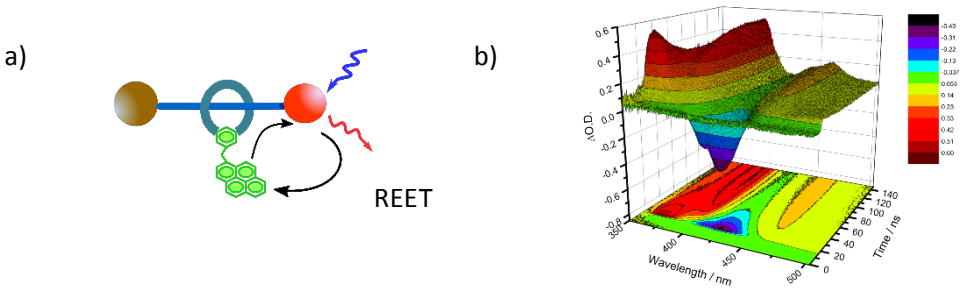

Figure 1 a) Cartoon representing reversible electronic energy transfer in a rotaxane prototype; b) transient absorption map showing real-time energy redistribution between chromophores.

ACKNOWLEDGEMENTSANR [grant n° ANR-16-CE29-0011], CSC.

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Excited state dynamics of protonated RNA/DNA bases in a cryogenically cooled ion trap: the case of uracil

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Photochemical damage to DNA by UV absorption is one of the main causes of a possible mutagenic effect affecting the genetic material.[1] It has been suggested that the excited state dynamics of these heterocycles has played a decisive role in the natural selection of the building blocks of life.[2] The excited state dynamics of DNA has indeed received much attention in the past thanks to the continuous advances in ultrafast spectroscopic techniques[3] and computational methodologies.[4]

The group has recently demonstrated that the full-time scale excited state dynamics can be followed up to milliseconds through an original pump−probe photodissociation scheme applied to cryogenic ion spectroscopy.[5-6-7] These spectroscopic studies rely on action spectroscopy, in which the absorption of a UV photon promotes the system in the excited state that ultimately leads to fragmentation. Cryogenic ion spectroscopy allows deciphering the lowest energy conformers through their energy-resolved vibronic spectra. Besides, cold ion traps offer the unique opportunity of extending the experimental time window for timeresolved dynamics over seconds as compared to what can be done for neutral molecules streamed in supersonic expansion.

In protonated cytosine,[8] the locally excited $^1\pi\pi^*$ state decays in the femtosecond range toward long-lived charge transfer and triplet states with lifetimes ranging from microseconds to milliseconds, respectively. A three-step mechanism ($^1\pi\pi^* \rightarrow {}^1CT \rightarrow {}^3\pi\pi^*$) has been proposed where internal conversion from each state can occur leading ultimately to fragmentation in the ground electronic state.

We are currently working on protonated uracil. The UV photodissociation spectrum consists of two sets of vibronic progressions reflecting the presence of two tautomers, which have been previously assigned to the excitation of the locally excited ππ* state that bears the oscillator strength for the UV excitation of the *keto* and *enol* tautomers of protonated uracil.[9] The locally excited state in these two systems have very different lifetimes: a few ns for the *keto* form and subpicosecond for the *enol* form, which is characterized by the line width broadening of the vibronic spectrum. However, the pump-probe and fragmentation kinetics experiments show the presence of a long-lived state for both tautomers, which could be associated to a triplet state ($^3\pi\pi^*$).

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Influence of the aggregation of metallic nanoparticles when coupled to photochromic molecules in hybrid systems

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Hybrid materials showing multiple photophysical properties have attracted considerable interest in the last few decades in the field of molecular electronics and photonic devices. Coupling plasmonics nanoparticles with photochromic molecules show many advantages such as enhanced optical and electromagnetic properties and molecular light switch control. Coupling these two units could lead to modulation of the surface plasmon resonance resonance under light irradiation [1] and an improvement of the photoswitching efficiency [2] at the same time due to crossed interactions between the plasmonic and the photochromic units. Such interactions can be increased when considering aggregated nanoparticles instead of isolated ones. [3]
Here we present hybrid nanosystems that highlight these crossed interactions. Moreover we will see how the aggregation state of gold nanoparticles could enhance these intercations. The enhancement of the local electromagnetic field induced by the aggregation process is studied using photo-emission electron microscopy (PEEM). This powerfull technic allows to map the near field intensity and localize it respect to the nanoparticles' organisation. [4]

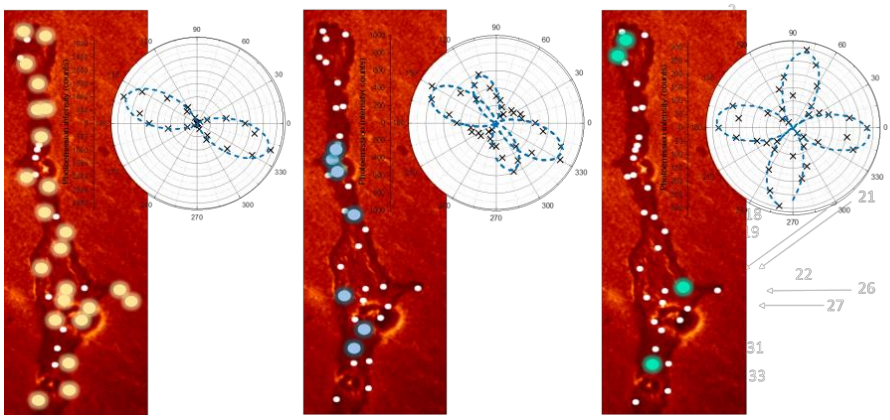

Figure 1 Images show the topography of aggregated gold nanorods and the localization of bright spots detected in photo-emission electron microscopy. Circular diagrams show the modulation of the photo-emission intensity when the polarization of the incident excitation laser is changed.

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Study of the liquid-liquid interface containing an extractant: Experiments and molecular dynamics modelling

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Ion separation by liquid-liquid extraction (LLE) is a process based on the difference in affinity of a solute between two phases that are not miscible with each other. In order to increase the affinity of the solute to be extracted, a transfer agent called extractant molecule is usually added. As LLE is the key to various industrial hydrometallurgical processes, a detailed knowledge of the supramolecular structuring of these interfaces containing amphiphilic-extracting molecules is essential for understanding this ion transfer phenomena. Unfortunately, experimental data allowing accessing to structural information from these interfaces are almost inexistent. For the first time the combination of x-ray and neutron reflectivity experiments made possible the access of these information.[1,2] The analysis of these measurements shows that trivalent cations can be repelled or attracted by an interface enriched with extractant depending on the nature of the molecule. The experimental structure observed being the result of the complex processing of many reflectivity data; it was interesting to see if molecular modelling (MD) could give comparable results without preliminary hypothesis on the surfactant. MD simulations of real solutions have been performed taking into account explicitly the polarization effects of all the atoms using the AMBER software.[3] The comparison of measurement and MD results supports not only the measurement and analysis of large instrument fates but also the parameters applied in MD simulations.

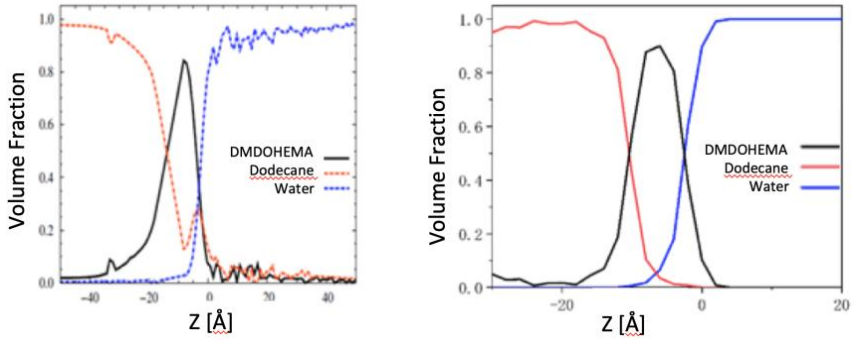

Figure 1 Experimental (left) and simulated (right) volume fractions of the extractant molecule (DMDOHEMA), water and dodecane versus depth.

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Quasi-Classical Simulation of Resonant Raman Spectra using Linearization in Molecular Dynamics

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Raman scattering is an optical process often used alongside infrared spectroscopy to provide structural information. Resonant Raman (RR) can be more specific because it relies on choosing the right incident radiation to excite the molecule in order to target specific transitions.
Resonant Raman however, often proves hard to compute: indeed, information on the nuclear dynamics in the electronically excited states is required.

We have developed a method based on a time-dependent representation of RR [1, 2] to retrieve this spectrum without resorting to heavy quantum computation of the nuclear dynamics. Through molecular dynamics, multiple trajectories are propagated over a mean potential surface [3] between the relevant excited state and the ground state. Forces on the atoms are then computed "on-the-fly".
Examples will be presented over simple model surfaces, and compared with quantum results (computed with a sum-over-state approach).

The method is also being implemented in an electronic computation code (CPMD package). To that end, a method to accelerate calculation of hybrid functionals [4] has also been implemented.

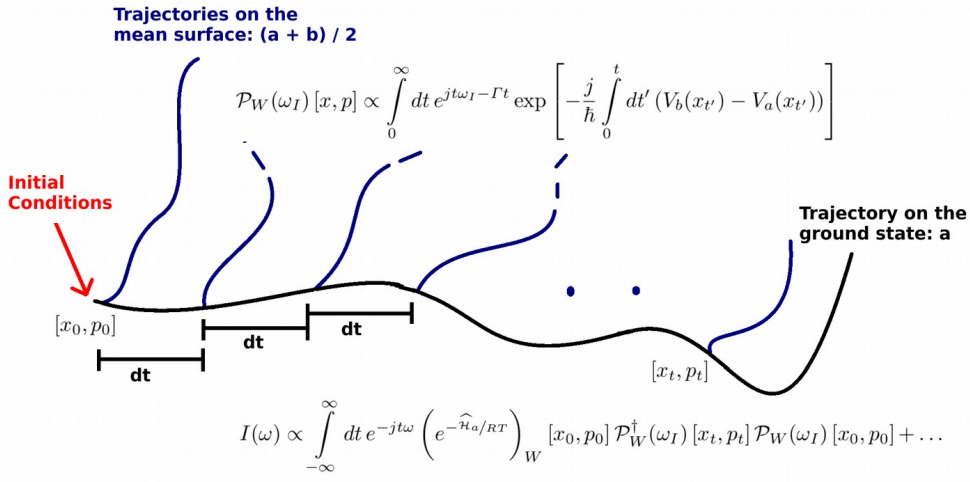

Figure 1 Scheme of the main algorithm

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Identification of ion pairs in solution by IR spectroscopy: crucial contributions of gas phase data and simulations

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In solution, an ion pair consists of a positive ion (cation, z^+) and a negative ion (anion, z^-) bonded together by the attractive electrostatic forces between them, forming a supramolecular neutral complex. Several types of ion pairs coexist: contact (CIP), solvent-shared (SIP) and solvent-separated (SSIP), in equilibrium with free ions (FI); their distribution depends on many parameters, and especially the ion concentration. Ion pairing occurs frequently in environments that are naturally rich in ions like seawater, inorganic atmospheric aerosol particles, or living organisms, and thus is of central importance in understanding chemical and biological processes in solution.

Ion pairing is suspected to be involved in many ion specific effects, but their characterization as well as their properties still remain mostly to be understood despite the numerous experiments carried out in solution during the past decades. In addition, theoretical chemistry approaches often struggle to establish a quantitative picture of ion pairing. A striking example of the difficulties encountered is illustrated by a recent set of studies on carboxylate anions paired with alkali metal cations which have led to inconsistent conclusions.[1,2]

Relying on IR spectroscopic experiments recently developed in our group on isolated neutral ion pairs,[3] we investigated carboxylate anions paired to alkali metal cations by using an original approach where gas phase results were used as an input to refine high level quantum chemistry calculations in solution, leading to an unprecedented level of accuracy in vibrational frequency prediction. First, gas phase experiments focused on a series of isolated contact ion pairs ([M^+, Ph-CH_2-COO^-] with M= Li, Na, K, Rb, Cs) for which UV and conformer-selective IR spectra were recorded. These experiments provided vibrational frequencies of the carboxylate stretch enabling us to assess the accuracy of mode-dependent scaled harmonic frequency calculations at the RI-B97-D3/dhf-TZVPP level. This level of calculation was then employed on large water clusters embedding a free acetate ion or its CIPs or SIPs with a sodium cation to obtain the individual vibrational spectra of these species in solution. These theoretical results show that the stretching modes of carboxylate are sensitive to both SIP and CIP formation. FT-IR spectroscopy confirms this finding since solutions of increasing concentrations exhibit spectral evolutions consistent with the presence of specific types of solvent-shared and contact ion pairs.

By providing relevant guidelines for the interpretation of solution phase IR spectra, this work illustrates the potential of the approach for the elucidation of supramolecular structures in electrolyte solutions.[4]

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Abiotic synthesis of RNA: towards an understanding of key molecular steps

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The emergence of life is one of the most fascinating and yet largely unsolved questions in the natural sciences, and thus a significant challenge for scientists from many disciplines. There is growing evidence that ribonucleic acid (RNA) polymers, which are capable of genetic information storage and self-catalysis, were involved in the early forms of life. But despite recent progress, RNA synthesis without biological machineries is very challenging. I will present some of our recent results that specifically address two major issues using a computational approach that relies on techniques ranging from quantum calculations to large-scale all-atom simulations, employed together with efficient enhanced-sampling algorithms. In particular, we aim to explain why the poorly-understood thermally-driven process of thermophoresis can contribute to the accumulation of dilute precursors; and to understand why linking RNA monomers with phosphoester bonds is so difficult, to understand the molecular mechanism of possible catalysts and to suggest key improvements of the current synthetic strategies.

Decipher the role of point defects on the optoelectronic properties of materials: the never ended story of TiS_2

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There has been an ongoing controversy on 1*T*-TiS_2's semimetallic[1] or semiconducting nature[2]for several decades due to the difficulty to synthetize stoichiometric TiS_2 and to predict its properties from computations. We tackle this issue by performing calculations on the CdI_2 layered structure type with the ideal 1:2 Ti:S stoichiometry using some of the most refined models, *e.g.* hybrid functional including Grimme's dispersion effects, the GW scheme and the Bethe-Salpether equation for the optical properties. All the calculations on the bulk (ideal) structure demonstrate that a (small) bandgap exists for the ideal material. Besides, van der Waals interactions must be taken into account during the calculation in order to reproduce accurately the TiS_2 structure, more precisely a correct c/a ratio. Then, for the first time we study point defects in the material using the same level of accuracy. These calculations demonstrate unambiguously that the most stable defect is the titanium interstitial located in an octahedral site inside the van der Waals gap. This point defect may explain the distinguishable electronic behavior of TiS_2 reported in the literature, *i.e.* non degenerated semiconductor (SC) or semimetal (SM) depending on defect concentration as a result of the synthesis conditions.[3,4]

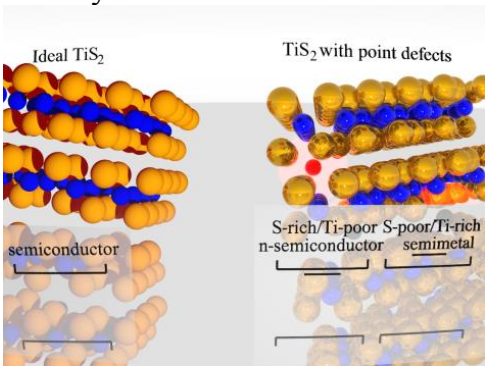

Figure 1 Schematic structure of pristine and doped (Ti_i) TiS_2.

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Astatinated mediated halogen bond in $X_3C–At^{\cdots}Z^-$ systems

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Astatine is a very rare radioactive element and little is known about its chemistry. Its 211 isotope is of great interest for the development of new cancers treatment (short half-life, α-emitter). Currently, the vectorization of astatine is planned *via* the formation of a R–At covalent bond with a biomolecule that can carry it to cancer cells. The development of efficient carriers is needed and the strong ability of astatine to give halogen-bond (XB) interactions[1] could be useful to improve the *in vivo* stability of the R–At systems.

In $X_3C–I\cdots Z^-$ halogen-bonded complexes with X and Z = F to I, an unexpected increase of the interaction strength has previously been emphasized, despite the weakened withdrawal effect of X.[2,3] Extending these series to $X_3C–At\cdots Z^-$ systems, scalar-relativistic DFT calculations firstly confirm these trends within the series X = F to I and Z = Cl, I and At. But, we additionally demonstrate that when X = At, a significant decrease of the interaction energies conversely arises, and that this decrease is even more important when the spin-dependent relativistic effects are taken into account. Relativistic effects, and especially the spin-orbit coupling (SOC) effects, are indeed known to play important roles in XB mediated by astatine,[4] and they contribute here to decrease the XB donating ability of $At_3C–At$ below that of $I_3C–I$, despite the higher polarizability of astatine. Our results illustrate the requirement to treat the relativistic SOC to assess the interactions involving astatine and to disclose the XB components.

ACKNOWLEDGMENTS

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Etats de spin nucléaire de l'eau : du confinement extrême en matrice de gaz rare au milieu interstellaire

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La découverte des « états de spin nucléaire » des molécules hydrogénées est contemporaine de l'apparition de la mécanique quantique. En raison du principe d'exclusion de Pauli, les molécules hydrogénées telles que H_2O ayant des atomes équivalents en positions interchangeables existent selon différentes configurations de spin "nucléaire" appelées *para* ou *ortho* selon la valeur du spin nucléaire total. Comme ces états de spin nucléaire sont en général très stables, l'échange d'une espèce vers l'autre (en basculant le spin de l'un ou plusieurs des atomes équivalents) n'est pas très favorisé dans la nature. Ces différentes familles de molécules peuvent être identifiées par leur signature spectroscopique infrarouge ou radiométrique. Elles sont observées dans différentes régions de l'espace par les télescopes spatiaux et au sol. Dans les queues de comètes comme dans le milieu interstellaire (*MIS*), le rapport d'abondance de ces « isomères de spin » (appelé *OPR* pour *Ortho-to-Para Ratio*) ne respecte pas toujours la valeur attendue à l'équilibre thermodynamique. Les astrophysiciens pensent que la valeur des OPR est très dépendante de l'environnement et de l'histoire des molécules (formation chimique, collisions réactives, cycles de d'adsorption/désorption des grains glacés, collisions non réactives). Le temps caractéristique de la Conversion de Spin Nucléaire (*CSN*) d'une espèce moléculaire vers l'autre à travers différents états de la matière (du plus confiné comme dans le solide au plus dilué comme dans la phase gazeuse) devient alors un facteur primordial pour l'interprétation des données observationnelles.

Nous présenterons les connaissances acquises lors d'une réanalyse récente des raies d'émission de l'eau provenant de la barre d'Orion et les travaux en cours pour comprendre et quantifier les mécanismes de rééquilibration des états de spin nucléaire dans les matrices de gaz rare et à l'interface glace-gaz.

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Discrimination chirale au sein de Dicétopiperazines

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Les Dicétopipérazines (DKP) résultent d'une liaison peptidique intramoléculaire formée après déshydratation d'un dipeptide linéaire. Ils sont étudiés depuis plusieurs années en raison de leurs similarités structurelles avec les peptides linéaires et de leur apparition dans les produits naturels biologiquement actifs.

La configuration absolue, L ou D, des différents résidus peptidiques peut influencer la structure du DKP. Il est donc intéressant de les étudier en phase gazeuse sous forme neutre pour les isoler d'un environnement. Pour cela, nous avons effectué des expériences combinant la spectroscopie laser avec une détente supersonique. Les spectres de double résonance IR-UV permettent d'identifier les signatures électroniques et vibrationnelles des différents conformères d'un système.[1] Des calculs de chimie quantique ont été effectués pour étayer les résultats expérimentaux. On a par exemple montré pour un DKP composé de deux L-Tyrosine[2] une compétition entre une structure de type « repliée-étendue » dans laquelle les deux résidus n'interagissent que par une interaction CH...π et une structure présentant une interaction de type OH…O entre les groupements hydroxyles. La structure liée par liaison hydrogène OH…O n'est pas observée pour un DKP hétérochiral (figure 1). Par ailleurs, seule la structure « repliée-étendue » existe dans un DKP composé de deux Phénylalanine[3]. Les deux diastéréomères diffèrent par la nature de l'interaction CH…π mise en jeu. Des résultats récents obtenus pour le DKP Tyrosine-Phenylalanine ou le DKP Tyrosine-Homo Serine pourront être discutés.

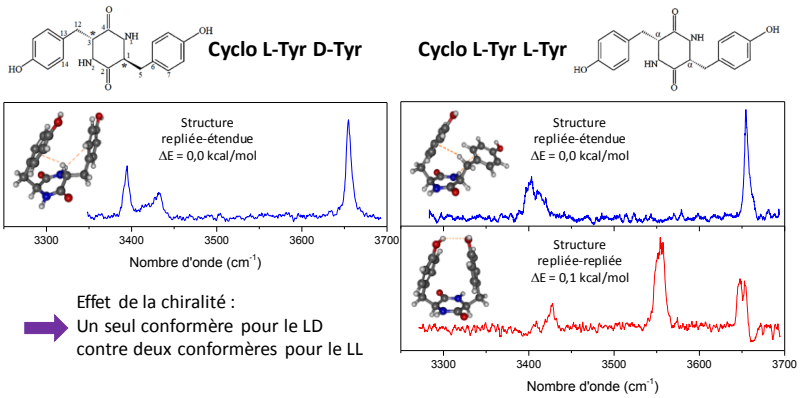

Figure 1 Comparaison des spectres vibrationnels et des structures calculées pour deux chiralités du DKP Tyr-Tyr

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Influence des rayonnements ionisants sur les complexes antibiotique/récepteur en phase gazeuse

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Les caractéristiques structurales des complexes non-covalents jouent un rôle primordial dans l'activité des molécules d'intérêt biologique, notamment la reconnaissance moléculaire entre un médicament et son récepteur. Ceci est illustré dans la figure 1, où l'on voit un antibiotique de la famille des glycopeptides, la Vancomycine, lié à son récepteur Ac_2-^{L}Lys-^{D}Ala-^{D}Ala en phase condensée, où les deux molécules sont fortement liées l'une à l'autre. En phase gazeuse, il a été montré que la structure native est conservée pour les espèces déprotonées mais pas pour les espèces protonées. [1,2]

Lors des traitements du cancer associant radiothérapie et chimiothérapie, les médicaments peuvent interagir avec les rayonnements ionisants. Afin de comprendre comment les interactions non-covalentes impliquées dans la reconnaissance moléculaire sont affectées par ces rayonnements, nous avons étudié la photoionisation de complexes protonés et déprotonés de la Vancomycine avec son récepteur en collaboration avec le groupe de T. Schlathölter (Université de Groningen, Pays-Bas), au moyen d'un spectromètre de masse couplé à des lignes de faisceau synchrotron. L'irradiation des systèmes moléculaires, sélectionnés selon leur rapport masse/charge, se fait dans un piège à ions, à température ambiante.

Après absorption d'un photon VUV par la Vancomycine isolée doublement protonée, on observe l'ionisation non dissociative (NDI), mais surtout la fragmentation du squelette peptidique ainsi que la rupture de la liaison glycosidique du groupement sucre, dues au transfert d'une partie de l'énergie du photon en énergie interne vibrationnelle. Cette énergie augmente avec l'énergie du photon, faisant disparaître le NDI aux énergies des rayons X. Pour le complexe doublement protoné Vancomycine/récepteur, la NDI n'est pas observée après la photo-absorption, probablement à cause de la faible énergie de liaison de ce complexe non-covalent. Ces systèmes moléculaires, lorsqu'ils sont doublement déprotonés, subissent le détachement d'un électron après photoabsorption, et le principal processus provoqué est la perte de CO_2, y compris pour le complexe, et ce sur toute la gamme d'énergie 14-30 eV. Nous avons donc constaté que dans ce cas, les liaisons non covalentes ne sont pas systématiquement rompues après la photoabsorption, ce qui est cohérent avec la grande énergie de liaison du complexe avec sa structure native, où le groupe CO_2 du récepteur est fortement lié à la poche de liaison de la Vancomycine. Nos résultats indiquent donc que l'état de protonation et la structure géométrique d'un complexe médicament-récepteur ont un effet important sur les processus induits par l'irradiation de photons dans la gamme d'énergie VUV-X. De plus, les interactions spécifiques de la reconnaissance moléculaire ne sont pas systématiquement perdues après la photoabsorption.

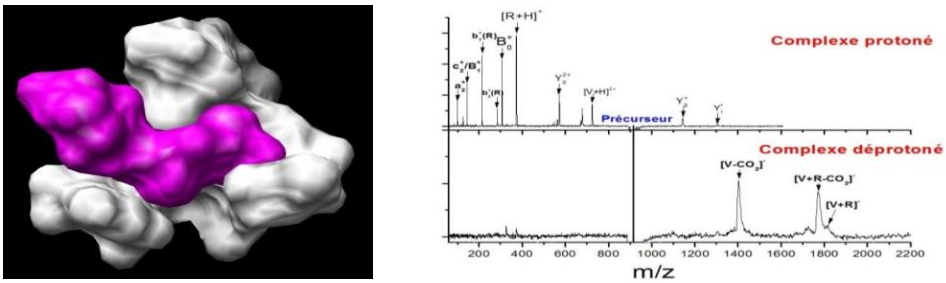

Figure 1 : à gauche : structure du complexe vancomycine (en blanc)/récepteur (en violet) (PDB 1FVM) ; à droite : spectres de masse du complexe vancomycine (V)/récepteur (R) doublement protoné (en haut) et déprotoné (en bas) après absorption d'un photon d'énergie 20 eV. Le rapport masse-sur-charge (m/z) du complexe non-irradié est indiqué par « précurseur », et les fragments viennent de la vancomycine sauf ceux notés $b_1^+(R)$ et $b_2^+(R)$. Les pertes de CO_2 de la vancomycine et du complexe après détachement d'un électron sont également indiquées.

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State-selected O_2^+ reactions with VUV synchrotron radiation for cold plasmas applications

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The measurements that will be presented are needed to refine the description of reactive astrophysical or industrial plasmas. They were recorded at SOLEIL synchrotron in the framework of a collaborative project aiming at a better description and optimization of industrial plasmas used for depollution of factory exhaust. To this end, the chemistry of ionic form of the major atmospheric species with main industrial pollutants has to be described. Here, molecular oxygen, O_2, has been used to produce O_2^+ molecular ions by photoionization. By means of TPEPICO coincidence methods they were prepared in selected, long-lived vibrational and electronic states ($X^2\Pi_g$, v=0-15 and $a^4\Pi_u$, v=0-4). Their reactivity with the propene molecule (CH_2=CH-CH_3) has been studied by varying the excitation energy and the collision energy and recording the absolute reaction cross sections for all ionic products.

Very contrasted results have been obtained, and, though they can be described in terms of charge transfer and dissociative charge transfer, specific sensitivity to the ionic state as well as to the collision energy has been observed, and will be discussed

These studies have been conducted on the CERISES set-up, a guided ion-beam experiment [1], with VUV radiation from the DESIRS beamline [2]. Recent developments of the CERISES setup allow for the production of new types of neutral precursors such as hydrocarbon radicals ($C_xH_y^\bullet$) and clusters (A_n) opening the possibility of new studies on the reactivity of their cations, $[C_xH_y^\bullet]^+$ and $[A_n]^+$, which include the comparison of the reactivity of different isomers or the effect of solvatation on the reactivity of cations. This enhances the offer on the chemistry of ions to external users of SOLEIL who can apply for beamtime with the CERISES setup through an association between our team and the SOLEIL synchrotron.

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Modélisation de la formation d'un plasma par laser dans le contexte de la fusion par confinement inertiel

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La fusion par confinement inertiel a pour objectif de comprimer par laser une cible d'hydrogène enrobée d'une couche de polystyrène afin de générer des réactions de fusion nucléaire. De nombreux processus physiques étant mis en jeu lors de l'implosion de la cible, des simulations numériques sont utilisées pour comprendre dans le détail cette physique de l'interaction et interpréter les résultats expérimentaux. Cependant, diverses hypothèses et approximations sont faites dans ces simulations. L'une d'elles est de supposer que toute la cible est instantanément portée à l'état plasma. Malgré le fait que cette hypothèse a permis de rendre compte de nombreux résultats expérimentaux, des expériences récentes suggèrent que la transition vers l'état plasma du polystyrène initialement solide, a tout de même une influence sur l'hydrodynamique ultérieure de la cible. La description de la transition de l'état solide de la coquille de polystyrène vers l'état plasma devient donc un sujet important.

Cette transition du polystyrène solide vers un plasma est induite par le chauffage laser. Ce dernier dépend des collisions des électrons libres qui ont été produits par le processus primaire de photo-ionisation. Le type de collision dépend de l'état de la matière, et par conséquent de sa température et densité. Pour une densité proche de la densité du solide, à basse température, le polystyrène est dans l'état solide et les électrons collisionnent avec les phonons du polystyrène. Le polystyrène étant un polymère, on peut supposer une périodicité locale et établir 3 modes propres vibrationnels, un mode acoustique et deux modes optiques. Les fréquences de collisions des électrons avec ces trois modes sont évaluées par calculs quantiques. A haute température, le polystyrène est complètement dissocié, le plasma se composant alors d'un mélange d'atomes de carbone et d'hydrogène partiellement ionisés. Les collisions électrons-atomes sont modélisées à partir de la section efficace classique de diffusion. Les collisions électron-ion sont décrites par un modèle adapté aux plasmas denses où le logarithme coulombien est modifié afin de rendre compte de l'effet d'écrantage.

Entre ces deux domaines limites, les espèces intermédiaires ont été identifiées afin de déterminer la nature et la valeur de la fréquence de collisions. On a ainsi mis en place un modèle de fragmentation du polystyrène en fonction de la température. Cette approche permet d'identifier les différentes étapes de dissociation du polystyrène jusqu'à la phase plasma. L'ensemble a permis d'obtenir un modèle de fréquence de collision valable de quelques dizaines de degrés kelvin jusqu'à la centaine de millions de degrés. Ce modèle permet alors de décrire l'absorption de l'énergie laser dans la cible lors de la transition de la coquille de l'état solide au plasma et de déterminer les conditions pour lesquelles cette transition a une influence sur la dynamique d'implosion de la cible.

Ammonia production and sticking on materials relevant to fusion reactors: tungsten and 316L stainless steel

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During ITER operation, it will be necessary to inject extrinsic impurities into the edge plasma to dissipate part of the plasma exhaust power through radiation. Nitrogen is one of the leading impurity candidates. NH_3 production has, however, been observed in the all-metal JET tokamak during N-seeding [1]. The formation of large quantities of tritiated ammonia has consequences for several aspects of the ITER plant operation in terms of tritium retention, gas reprocessing and duty cycle. It is currently unclear how and where ammonia is formed in fusion devices. In this contribution, we address the following questions: what is the dominant ammonia formation mechanism and what is the sticking probability of ammonia molecules on ITER-relevant material?

Our studies are performed in ultra-high-vacuum [2] using ion beam and molecular beam exposure of polycrystalline tungsten and stainless steel (SS316L) samples. To understand the mechanism of ammonia formation, sequential implantation of N_2^+ and D_2^+ at room temperature is performed and Temperature Programmed Desorption (TPD) is used to quantify HD, D_2, N_2 and ND_3 production rates. We show that deuterated ammonia (ND_3) is produced on both metals when bulk deuterium (D) diffusion is activated. On the other hand, the absolute quantity of ND_3 produced is found to be strongly dependent on the sample material. This difference in ND_3 production rate is related to dissimilarities in the formation process. On polycrystalline tungsten, the formation mechanism involves the implanted N atoms that are present at the surface. Nitrogen implanted deeper is unable to participate in the production of ND_3. In stark contrast, on SS316L, N atoms naturally contained in the bulk alloy participate significantly in the formation of ND_3 through diffusion to the surface, which occurs at the temperatures investigated here.

Finally, the absolute sticking probabilities of NH_3 molecules on tungsten and SS316L surfaces have been measured as a function of surface temperature and NH_3 kinetic energy revealing a molecular adsorption on both surfaces. NH_3 dissociation is found to be negligible below 450 K as seen by *in situ* Auger electron spectroscopy. A distribution of NH_3 desorption energy is measured resulting in a significant release of NH_3 at room temperature for both surfaces.

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Investigation of CH_3I and CH_3I-H_2O by matrix-isolation FTIR spectroscopy

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Iodomethane i.e. CH_3I (^{131}**I**) can be found inside the containment of a pressurized water reactor (PWR) following a severe nuclear accident (Chernobyl, Fukushima…) and further it can be transported into the atmosphere in the case of a containment leakage [1]. In the atmosphere, CH_3I may interact with atmospheric species such as water droplets or aerosols, which may influence their environmental and sanitary impacts. The investigation of water-CH_3I interaction is a first step to better understand the molecular interaction of CH_3I with hydrated aerosols. In this context, we have studied the formation of CH_3I clusters and CH_3I-H_2O complex using the matrix-isolation FTIR technique.

Gaseous CH_3I (1000 ppm) diluted in Ar or pre-mixed samples of CH_3I/Ar/H_2O were deposited in a vacuum chamber on a NaCl window for 2 hours and cooled at 10K. Gas isolated samples were measured with an FTIR spectrometer. Additionally, to study the interaction of both CH_3I and CH_3I-H_2O with sea salt aerosols, a first balloon with 1g of dry NaCl was filled with CH_3I and a second balloon containing 5.18 g of wet NaCl saturated with water (2 ml) was filled with CH_3I. NaCl powder was analyzed by DRIFTS after CH_3I exposure.

The FTIR spectrum of CH_3I in matrix clearly showed peaks for both CH_3I monomer and dimer as described in the literature [3]. The FTIR spectrum of CH_3I-H_2O mixtures showed peaks for CH_3I monomer, CH_3I dimer, CH_3I-H_2O complex and new xCH_3I-yH_2O complexes. Similar spectra were observed in the gas phase in the presence of both wet and dry NaCl. However, DRIFT spectra of NaCl exposed to CH_3I showed a clear dominant peak at 1085 cm^{-1} which can be assigned to the bending of CH_2 [2]. This new IR band reveals ~~a~~ formation of CH_3I-derived compounds strongly bonded to the NaCl surface that may affect the cycle life of iodine in the atmosphere.

The IR peaks assignment of the $_xCH_3I$-yH_2O complex will be further assigned with the help of theoretical calculations.

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Digitizing gold porous electrodes using FIB-SEM analysis

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Abstract : This project is dedicated to a bottom-up approach to optimize the design of porous electrode materials devoted to biofuel cells and biosensors. These devices operate on the basis of complex enzymatic electrochemical redox reactions coupled to mass transfer of substrates (glucose and O_2) and electron transfer within the pores of the structure and from/to the pore surfaces. The advantage of using porous materials for these devices lies in the very large internal surface area (where electron exchange takes place) to overall material volume ratio, yielding much larger current densities than on a bare solid electrode of the same size. Some very interesting techniques, based on templating silica beads on gold substrate with a Langmuir-Blodgett deposition[1] step followed by electroplating of gold[2] and beads dissolution have been elaborated to synthetize porous materials made of pure gold having a typical spherical pore size of the order of the micrometer. The objective of the project is to model the porous structure of the electrode. First, a determination of the geometrical characteristics can be achieved through image acquisition and analysis. The structure not only contains a gradient of hollow spherical pore radii, but also some degree of disorder due to local arrangement defects; the radii of the windows separating the pores is also locally variable. Since pore window dimensions are around 100 nm, Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM[3]) **(Fig. 1)** has been performed to obtain a 3D reconstruction of the porous medium. Segmentation and binarization of images were made both manually and automatically using Fiji and Python. More than 600 SEM (SE) images (25 nm between 2 images) yield a 3D image of a part of the electrode **(Fig. 2)**. The shape of the connections between spheres, the distances between spheres and the sphere diameters have been analysed.

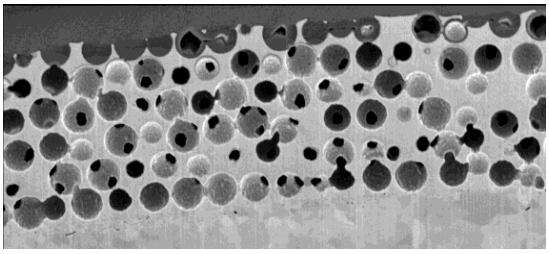

Fig. 1 : example of FIB-SEM image of the porous gold electrode

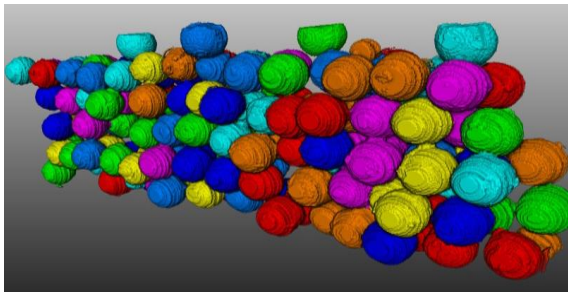

Fig. 2 : 3D reconstruction of the void space of a part of the porous medium

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Adsorption and Thermodynamics Study of Inhibition of Corrosion the AINSI 316L Stainless steel in HCl Medium Using carboxylic acids

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Abstract:

Austenitic stainless steels are widely used in medical and pharmaceutical industrial activities. This steel is an alloy sensitive to localized corrosion, especially pitting, which is one of the most dangerous forms, when exposed to aggressive ions. Corrosion can cause significant economic losses and serious damages (even major accidents), which involves many fields in daily life and industries. For example, the direct cost of metallic corrosion is estimated to be up to $2.2 trillion annually worldwide and about $270 billion in the USA alone [**1,2**].

In this work, inhibitive and adsorptive properties of Carboxylic acids for the corrosion of Stainless steel in 0.5 M HCl solutions was investigated using weight loss (WL), open circuit potential (OCP), potentiodynamic polarization method, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) analysis. The result has proved that the extract is a good inhibitor of corrosion of stainless steel in HCl. The Inhibition efficiency of three inhibitors decreased as temperature and time of immersion increased but increased with increase in concentration of carboxylic acids. Data were examined by fitting to several adsorption isotherms including Langmuir, Langmuir modified, EL-Awwadi, Temkin, Freundlich, The R2 values of 0.997 and 0.965 indicate strong adherence to Langmuir modified adsorption isotherm.

Keywords: Adsorption; Corrosion; Stainless steel; Inhibition; Carboxylic acids.

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Molécules et matériaux mécanofluorochromes comme sondes locales de contraintes

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Un matériau mécanofluorochrome est un matériau fluorescent sensible aux forces mécaniques (compression, cisaillement…). Ce type de matériau, moléculaire ou polymère, attire une attention croissante et différents composés mécanofluorochromes ont été préparés. [1] Toutefois, les études existantes sont souvent qualitatives : ni la nature de la force appliquée pour obtenir le changement de fluorescence ni son intensité ne sont connues. Notre objectif est de mesurer des contraintes mécaniques en utilisant des matériaux mécanofluorochromes, ce qui dans un premier temps requière une meilleure compréhension des relations structure / propriétés mécanofluorochromes. Nous nous intéressons en particulier à une famille de complexes difluorure de bore à ligand dicétone (figure 1). [2] Les propriétés photophysiques de ces matériaux moléculaires avant et après contrainte mécanique seront présentées.

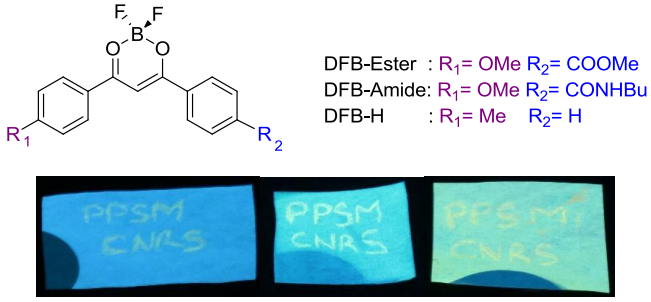

Figure 1. A. Complexes de bore-dicétone synthétisés. B. Clichés des films recuits de **DFB-H** (gauche) **DFB-ester** (centre) et **DFB-amide** (droite) (excitation 365 nm). PPSM CNRS inscrit à l'aide d'une spatule en utilisant les propriétés mécanofluorochromes des films.

ACKNOWLEDGMENTS:

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Patterning of the surface electrical potential on chalcogenide glasses by thermal poling

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Due to their transparency in the far and mid-infrared spectra, chalcogenide glasses (ChG) have become a highly promising material for the development of sensing devices. Recent studies[1,2] have shown the possibility to locally modify the optical properties of such materials by a thermoelectrical imprinting process (thermal poling). In the present work, we employed this method to micropattern the surface electrical potential of a ChG. For the ternary system Ge-Sb-S, different glass compositions were prepared in order to evaluate the effects of the sulfur stoichiometry. After the thermal poling, the samples were characterized via vibrational spectroscopy (IR and Raman) to observe structural modifications while the surface electrical potential was measured by Kelvin Probe Force Microscopy (KPFM). Raman imaging results suggest the depletion of sodium cations in the electrically polarized zones, leading to the accumulation of non-compensated charges on those areas. Effective surface patterning was then confirmed by KPFM, as positively and negatively charged zones matching the motifs of the electrodes were observed. Furthermore, these electrical patterns could still be seen after long-term storage (~24 months), showing significant stability over time. Interestingly, these modifications of the electrical potential were more significant for the stoichiometric composition compared to the samples with an over stoichiometric amount of sulfur. We observed that the surplus in sulfur leads to the formation of S-S chains and rings which might be responsible for charge dissipation effects on those compositions. Our results demonstrate the possibility to perform multi- functionalization (optical and electrical) of chalcogenide glasses, paving the way for their integration into novel sensing systems.

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Synthèse chimique et caractérisation du copolymère poly (orthométhoxyaniline-co-orthotoluidine) : application en tant qu'inhibiteur de corrosion de l'acier au carbone dans le milieu NaCl 3%.

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RESUMÉ:
Les polymères conducteurs ont été largement étudiés en raison de leur pouvoir conducteur du courant ainsi que de leurs propriétés physico-chimiques. Ils sont appliqués dans plusieurs domaines notamment dans l'inhibition et la protection des métaux contre la corrosion. L'un des facteurs qui freine les applications des polymères conducteurs est l'insolubilité de ces matériaux dans les milieux aqueux ou organique, ainsi de nombreuses recherches se sont focalisées sur l'étude de la solubilité des polymères conjugués [1].
Dans ce travail, on s'intéresse en premier lieu a la synthèse chimique d'un copolymère conducteur soluble poly (orthométhoxyaniline-co-orthotoluidine) à base de deux monomères (orthométhoxyaniline et orthotoluidine). Puis, ce copolymère est caractérisé par différentes techniques. Par la suite, l'étude sera consacrée à l'utilisation de ce copolymère comme inhibiteur de corrosion de l'acier au carbone dans le milieu NaCl 3%. Cette étude est réalisée par des mesures potentiodynamiques et d'impédance électrochimique en utilisant une électrode en acier à disque tournant. Les résultats obtenus ont montré que les courants cathodiques et anodiques sont affectés par l'ajout du copolymère, par conséquent, l'action inhibitrice de ce copolymère est de type mixte. Le phénomène d'adsorption de cet inhibiteur a été mis en évidence par les mesures d'impédance électrochimiques. L'efficacité inhibitrice augmente proportionnellement avec la concentration en inhibiteur tout en restant dans la gamme des faibles concentrations. En outre, la vitesse de rotation présente un effet bénéfique de l'hydrodynamique sur l'adsorption de ce copolymère sur la surface de l'acier au carbone ce qui entraine une bonne protection contre la corrosion.

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Etude des états excites formés par photoexcitation de composites zeolite / dicyano-anthracène

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Les propriétés électroniques et photoniques des cristaux moléculaires dépendent fortement de l'organisation structurale et spatiale des chromophores qui le composent. Le contrôle du polymorphisme offre ainsi une voie de modulation et d'optimisation des propriétés de ces composés moléculaires organiques en vue de leurs applications. Dans cette optique, la cristallisation de couches organiques à la surface de matériaux zéolitiques est attractive. En effet, d'une part, la nano-structuration de la surface zéolithes est susceptible de contraindre et d'orienter les molécules organiques adsorbées, et d'autre part, les propriétés électrostatiques et électroniques des zéolithes, ou encore la possibilités de les fonctionnaliser par insertion de molécules hôtes dans le volume poreux, sont autant de possibilités de designer de composites mixtes organiques-inorganiques photo-actifs.

Dans cette perspective nouvelle d'application des zéolithes, nous présentons une étude des états excités formés par photoexcitation de molécules de dicyano-anthracène (DCA), cristallisées à la surface de cristaux de zéolithes ZSM5. Les états excités formés par photoexcitation du composite DCA-ZSM5 ont été caractérisés par spectroscopie d'émission ps (TCSPC), et spectroscopie de vibration infrarouge fs. Les résultats obtenus montrent la formation ultrarapide (< 200 fs) d'au moins trois types d'espèces, pouvant être identifiées au moyen de la fréquence de vibration associée au mode d'élongation de la liaison CN, qui est fortement sensible à la distribution des charges de la molécule. Des calculs TD-DFT des états excités du DCA appuient l'attribution empiriques des bandes de vibration. Des données similaires ont été obtenues pour les cristaux de DCA purs, pour lesquelles, par rapport au composite DCA-ZSM5, nos résultats montrent une nette modification de la distribution des espèces initialement formées.

En conclusion, ces premiers résultats valident l'application de la spectroscopie de vibration transitoire pour l'identification des espèces excitoniques, les états de charge séparée et les excimères formés dans des composites à base de zéolite, et démontrent que la cristallisation de molécules organiques en surface des zéolithes permet de modifier de façon notable la photophysique du composé organique.

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Identification of ion pairs in solution by IR spectroscopy: crucial contributions of gas phase data and simulations

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In solution, an ion pair consists of a positive ion (cation, z^+) and a negative ion (anion, z^-) bonded together by the attractive electrostatic forces between them, forming a supramolecular neutral complex. Several types of ion pairs coexist: contact (CIP), solvent-shared (SIP) and solvent-separated (SSIP), in equilibrium with free ions (FI); their distribution depends on many parameters, and especially the ion concentration. Ion pairing occurs frequently in environments that are naturally rich in ions like seawater, inorganic atmospheric aerosol particles, or living organisms, and thus is of central importance in understanding chemical and biological processes in solution.

Ion pairing is suspected to be involved in many ion specific effects, but their characterization as well as their properties still remain mostly to be understood despite the numerous experiments carried out in solution during the past decades. In addition, theoretical chemistry approaches often struggle to establish a quantitative picture of ion pairing. A striking example of the difficulties encountered is illustrated by a recent set of studies on carboxylate anions paired with alkali metal cations which have led to inconsistent conclusions.[1,2]

Relying on IR spectroscopic experiments recently developed in our group on isolated neutral ion pairs,[3] we investigated carboxylate anions paired to alkali metal cations by using an original approach where gas phase results were used as an input to refine high level quantum chemistry calculations in solution, leading to an unprecedented level of accuracy in vibrational frequency prediction. First, gas phase experiments focused on a series of isolated contact ion pairs ($[M^+, Ph\text{-}CH_2^-COO^-]$ with M= Li, Na, K, Rb, Cs) for which UV and conformer-selective IR spectra were recorded. These experiments provided vibrational frequencies of the carboxylate stretch enabling us to assess the accuracy of mode-dependent scaled harmonic frequency calculations at the RI-B97-D3/dhf-TZVPP level. This level of calculation was then employed on large water clusters embedding a free acetate ion or its CIPs or SIPs with a sodium cation to obtain the individual vibrational spectra of these species in solution. These theoretical results show that the stretching modes of carboxylate are sensitive to both SIP and CIP formation. FT-IR spectroscopy confirms this finding since solutions of increasing concentrations exhibit spectral evolutions consistent with the presence of specific types of solvent-shared and contact ion pairs.

By providing relevant guidelines for the interpretation of solution phase IR spectra, this work illustrates the potential of the approach for the elucidation of supramolecular structures in electrolyte solutions.[4]

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Etudes de dicétopipérazines par spectroscopies

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Les dicétopipérazines (DKP) sont des molécules d'intérêt thérapeutique formées par condensation d'un dipeptide linéaire. Les configurations absolues, L ou D, des résidus d'acides aminés peuvent influencer les conformations adoptées par les DKP. Il est donc intéressant d'étudier ces conformations pour différents stéréoisomères. Ceci peut être réalisé par des méthodes spectroscopiques en phase gazeuse et en phase condensée. La spectroscopie laser électronique et vibrationnelle sélective en conformères en phase gazeuse et le dichroïsme circulaire vibrationnel en phase condensée sont utilisés à l'ISMO.
L'équipe a montré que les effets de chiralité sont importants pour la molécule de cyclo-[tyrosine-tyrosine] (c-Tyr-Tyr) en phase gazeuse.[1] En effet, c-LTyr-LTyr et c-LTyr-DTyr présentent une conformation semblable, dite « repliée-étendue », mais c-LTyr-LTyr présente une conformation stable supplémentaire radicalement différente, avec une liaison hydrogène O-H···O (**Figure 1,** a). Cependant, seule la conformation « repliée-étendue » est stable pour les diastéréoisomères de la cyclo-[phénylalanine-phénylalanine] (c-Phe-Phe) en phase gazeuse.[2] L'équipe a par ailleurs étudié c-Phe-Phe en phase solide, et a ainsi prouvé la formation de dimères.[3]

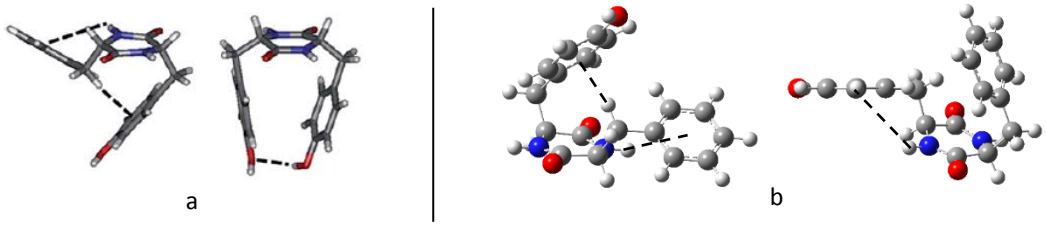

Figure 1 Conformations observées de c-LTyr-LTyr (a) et de c-LTyr-LPhe (b)

La molécule de cyclo-[tyrosine-phénylalanine] (c-Tyr-Phe) a été récemment étudiée en phase gazeuse pour vérifier l'éventuelle existence d'une interaction O-H···π dans c-LTyr-LPhe. On a alors montré que cette interaction est absente, et que les diastéréoisomères possèdent chacun deux conformations stables (Tyr repliée-Phe étendue et vice-versa) (**Figure 1**, b). Les diastéréoisomères diffèrent alors seulement par la nature de l'interaction C-H···π et par la force de la liaison N-H···π. Le dichroïsme circulaire vibrationnel est en cours pour cette molécule. Les résultats sur cette molécule seront présentés.

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Influence de l'erreur de self-interaction sur la structure électronique et géométrique de radicaux

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De très nombreux processus chimiques impliquent la formation d'intermédiaires ayant reçu ou cédé un électron. Du fait de leur caractère transitoire, la structure électronique de ces radicaux est souvent mal connue. De plus, les méthodes de modélisation les plus standards, telle que la DFT, ne sont pas en mesure de décrire convenablement la structure électronique de ces espèces du fait de l'erreur de self-interaction.

Lors de travaux antérieurs, nous avons montré les difficultés de la DFT pour décrire convenablement la structure électronique de peptides réduits en phase gazeuse. Les fonctionnelles corrigées à longue portée (LC-DFT) apportent une réponse seulement partielle à ce problème puisque selon le système étudié et la quantité d'échange Hartree-Fock incluse dans la fonctionnelle, les résultats peuvent varier.[1]

Plus récemment, nous nous sommes intéressés à la structure de composés aromatiques azotés après mono-réduction électronique, ces molécules pouvant par exemple servir de réservoir à électron dans des complexes organométalliques. Sur ces composés, une gamme variée de méthodes de modélisation a commencé à être utilisée avec deux objectifs : (*i*) obtenir des données théoriques de référence, par exemple avec des calculs Coupled-Cluster ou avec la méthode FOBO-SCF, basée sur une approche *ab initio* de type interaction de configuration et développée récemment pour calculer de façon extrêmement précise la densité de spin dans des molécules à couche ouverte;[2] (*ii*) estimer la pertinence de méthodes a priori moins précises mais rapides, telle que la DFTB, éventuellement contrainte et couplée avec l'interaction de configuration,[3] méthodes qui permettraient d'aborder des systèmes de plus grande taille. Les premiers résultats obtenus avec ces différentes méthodes seront présentés.

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Nouvelle méthode de révélation d'empreintes digitales sur scène de crime

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L'utilisation des empreintes digitales joue aujourd'hui un rôle clé dans l'identification d'un individu. Les techniques actuelles ne permettent pas toujours de rendre visibles et accessibles ces empreintes aux forces de l'ordre. La fumigation du cyanoacrylate reste à ce jour la méthode la plus largement employée par celles-ci pour révéler les traces latentes (sur les scènes de crime). Cependant, cette méthode nécessite une chambre de fumigation, environnement à la fois confiné et contrôlé qui limite son utilisation à de petits objets emportés au laboratoire. C'est dans ce contexte que s'inscrit le projet ANR Cyanospray dont l'enjeu est de développer une nouvelle méthode de révélation plus simple et efficace par brumisation d'un mélange aux propriétés fluorescentes. Et le présent travail s'attache à répondre à ce besoin via une technologie à l'application concrète et opérationnelle.
La première étape a été de s'affranchir de la variabilité des empreintes qui dépend du donneur (forme et composition) mais aussi de l'âge du dépôt. Dans ces conditions, une nouvelle méthode de déposition d'empreintes digitales artificielles par micro-impression a été développée. Ce modèle, de forme et de composition contrôlées, trouve toute son importance dans la comparaison de paramètres physico chimiques dans la mesure où ces derniers influencent la qualité de l'empreinte révélée. En effet, l'utilisation d'un procédé de révélation par brumisation de réactif fluorescent se révèle complexe et dépendant de paramètres physico chimiques variés tels que l'humidité ambiante ou encore la température.
Par la suite, l'accent a été mis sur la compréhension de ce système complexe à travers le couplage de multiples techniques analytiques. A ce titre, l'imagerie infrarouge ainsi que la microscopie confocale de fluorescence ont permis d'offrir de larges possibilités pour comprendre comment s'organise notre réactif fluorescent au sein même de l'empreinte, ainsi que son évolution au cours du temps. Par ce biais, une analyse multidimensionnelle a pu être réalisée ouvrant ainsi de nouvelles possibilités de caractérisations non destructives d'un système métastable et évolutif tel que les empreintes digitales.

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Chemical fingerprint of sewage sludge : combination of target, suspect and non target analysis

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Human activities release a wide range of micropollutants (MPs) in the sewage network and consequently discharge them to sewage treatment plant (WWTP). A part of this MPs are treated by the treatment processes. However, the reduction of MPs load in the treated effluents is not directly related to the degradation of these compounds. Indeed, a part of these molecules could be transformed and/or trapped, and so accumulated in sewage sludges. Thus, the use of sludges as fertilizer in agriculture may act as an additional MP source for soil and aquatic ecosystems (after water runoff or infiltration). A better chemical characterisation of sludge obtained by various processes is thus necessary and could help to predict the potential associated release of MPs in the environment and finally the associated risks for wildlife.
For this purpose, a chemical screening was performed on thirty different sludges originating from various treatment processes (*e.g.* activated sludge, planted reeds, membrane bioreactor, sequencing batch reactor…). The most exhaustive screening of MPs possible, based on target, suspect and non-target analyses, has been carried out out by liquid and gas phase chromatography coupled to tandem mass spectrometry (MS/MS) and high resolution mass spectrometry (HRMS – QTOF technology). For the target and the suspect approaches, 57 pollutants belonging to different classes (*e.g.*, detergents, personal care products, perfluorinated compounds, plasticizers, flame retardants...) were screened and quantified. The list was established on various criteria such as occurrence, relevance, toxicity, regulations, …. In parallel the non target approach was undertaken to enlarge the spectrum of screened compounds using a non a priori strategy.
Phtalates, alkylphenols, perfluorinated compounds, hexabromocyclododecanes, and chloroalkanes have been detected by target analysis in several sludges, with phtalates and alkylpenols as predominant families among the observed molecules. In addition the suspect mode has brought 21 more molecules among them personal care products (musk, UV filters, antioxidants, biocides). The non target analyses have allowed establishing an overall contamination profile for each sample. The results showed the detection of thousands features in each sludge. Among these detected entities, untargeted compound classes such as polycyclic aromatics hydrocarbons, several pharmaceuticals, pesticides, steroids and transformation products have been put in evidence. The chemical fingerprints of samples were also compared by statistical means. This comparison allowed discriminating a treatment (planted reeds) as a potential promising process to reduce the number of compounds in sewage sludge.

ACKNOWLEDGMENTS

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Inventaire radiolytique dans l'eau soumise à des impulsions d'électrons femtoseconde produits par laser de haute intensité

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Les effets radiobiologiques de la nouvelle et prometteuse méthode FLASH de radiothérapie par des électrons pulsés de durée µs semblent être liés à un effet de débit de dose [1]. Cet effet pourrait être exacerbé en utilisant des débits de dose bien plus élevés. Aussi, nous décrirons dans cette présentation les effets chimiques provoqués par des impulsions ultrabrèves (10^{-15} s = femtoseconde) d'électrons produites par des champs laser ultra intenses (10^{18} W/cm^2). C'est le domaine des débits de dose ultimes, soit, des TGy/s (Tera Gray/s = 10^{12} J.kg^{-1}.s^{-1}).

Les rendements radiolytiques que nous redéfinirons ici, sont la résultante, d'une chimie complexe opérée dans les grappes d'ionisations par les radicaux libres de l'eau [2] issus de l'ionisation de molécules d'eau exposées à une bouffée de rayonnement d'électrons de plusieurs dizaines de MeV regroupés en paquet d'une durée de quelques femtosecondes et surgissant d'une cellule remplie d'hydrogène, illuminée par un flash laser d'une très grande intensité [3].

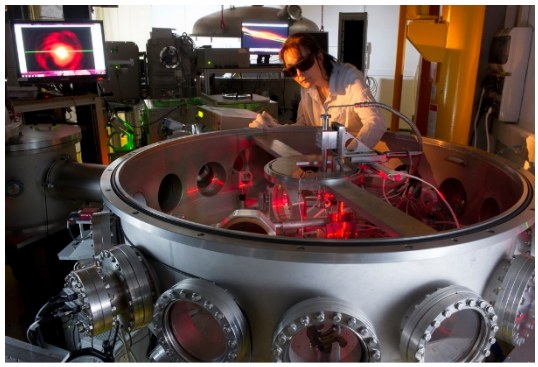

Figure 1 Vue de l'enceinte d'interaction de l'installation laser UHI100 au CEA Paris Saclay

Nous verrons que les électrons hydratés, les radicaux hydroxyle et le peroxide d'hydrogène ne sont pas formés dans les proportions habituelles, celles rencontrées lors d'irradiation par des débits de dose faibles (d'une source gamma, par exemple). Nous proposerons un modèle de l'interaction de ces impulsions d'électrons avec l'eau et nous nous projèterons dans le monde cellulaire où tant d'autres édifices moléculaires (protéines, ADN, membranes,...) sont prêts à interagir directement ou indirectement avec ce paquet d'électrons.

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Action spectroscopy of isolated polyalanine peptide ions in the VUV

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Since the introduction of electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI), systems larger than previously could be placed in the gas phase and analyzed by mass spectrometry. Gaseous ions may be sorted according to their mass to charge ratio and stored in traps. These ions may then be interrogated by various means. Usually, the confinement of selected ions is not sufficient to allow measuring the attenuation of incoming particle beams such as in classical spectroscopic schemes. However, the interrogation of stored ions provides valuable information on the consequences of the interaction with the probe particle simply by measuring mass spectra. Measurement of mass spectra as a function of the photon wavelength allows to perform action spectroscopy on the selected target [1-3].

Here we report a spectroscopic study of polyalanine peptides in the vacuum ultraviolet using the coupling of a linear ion trap with the DESIRS beamline at SOLEIL.

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Caractérisation théorique des propriétés antioxydantes de flavonoïdes.

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Les flavonoïdes sont des composés de la famille des polyphénols naturellement présents en abondance dans les végétaux. Les flavonoïdes d'origine naturelle possèdent un intérêt industriel majeur car ils sont de puissants agents antioxydants avec des applications potentielles dans les domaines de l'agroalimentaire et de la nutraceutique, mais également en cosmétique et pharmaceutique. Un grand nombre de leurs effets biologiques semble être lié à leur capacité à moduler certaines cascades de signalisation cellulaire. Leurs propriétés anti-inflammatoires, anti-thrombogènes, antidiabétiques, anti-cancéreuses et neuroprotectrices ont ainsi été mises en évidence.

Le projet FunRégiOx a pour principal objectif le développement d'un procédé rationnel novateur, applicable dans les industries agroalimentaire et biotechnologique, pour la glycosylation "à façon" de flavonoïdes par des approches de chimie enzymatique. La sélection des flavonoïdes à fonctionnaliser nécessite au préalable de bien appréhender les composés présentant a priori les meilleures propriétés antioxydantes. Dans cette perspective, nous avons mis en œuvre des calculs DFT permettant de modéliser les différents mécanismes d'activité antioxydante possibles : HAT, transfert d'atome d'hydrogène, SET-PT, transfert d'électron suivi d'un transfert de proton, et SPLET, extraction de proton suivi d'un transfert d'électron. Ces études théoriques ont été réalisées au niveau M06-2X/6-311++G(d,p), récemment utilisé dans ce contexte.[1,2] Ces processus pouvant avoir lieu dans l'organisme indifféremment au sein de liquides physiologiques ou des membranes lipidiques, ces environnements ont été modélisés en plongeant les solutés étudiés dans un continuum d'eau et de benzène, respectivement, à l'aide de la méthode SMD.[3] Ainsi, l'influence du milieu sur le mécanisme d'oxydation et sur le site réactionnel a pu être mise en évidence, tout comme l'influence de la glycosylation régiosélective.

REMERCIEMENTS

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Myoglobine dans un mélange eau+liquides ioniques.

Ou comment on redirige l'activité de l'hémoprotéine vers un centre d'activation pour la réduction du dioxygène

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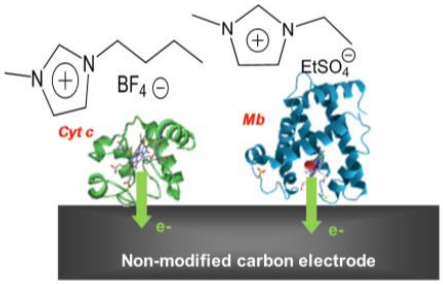
Un transfert électronique direct (i.e. sans médiateur) entre une protéine redox et une électrode constitue un aspect important à la fois du point de vue fondamental (étude des propriétés redox des biomolécules) et appliqué (développement de biocapteurs, biopiles et systèmes bioélectroniques).[1,2] Cependant, cela nécessite souvent une modification appropriée de la surface d'électrodes. Nous avons démontré qu'un transfert d'électron direct et rapide entre une électrode de carbone vitreux nue et des hémoprotéines (myoglobine, hémoglobine et cytochrome c) est facilement détecté lorsque l'on utilise un électrolyte concentré composé d'un mélange d'eau et de liquides ioniques à base de cations imidazolium.[3]

Le liquide ionique joue un rôle clé dans ce comportement. De plus, dans ce milieu non conventionnel, il est possible de rediriger l'activité de la myoglobine, qui fixe l'oxygène dans les tissus, vers une activité catalytique d'activation du dioxygène. Les interactions entre liquides ioniques et protéines restent à ce jour mal comprises [4] Pour rationaliser le phénomène, des études combinant des analyses électrochimiques à des études spectroscopiques (RMN, FTIR, UV-vis) et des simulations de dynamique moléculaire ont été menées. Ces études démontrent que le mélange liquides ioniques/H_2O induit des modifications localisées et réversibles de la conformation des protéines, en particulier la structure secondaire de la myoglobine évaluée par ATR-FTIR montre des variations structurales intéressantes.



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Beyond the Standard Statistical Approach of Chemical Reaction Dynamics:

The Chaotic Dynamics Model.

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We present the chaotic dynamics model (CDM) which we have developed recently to go beyond the standard statistical approach for complex-forming atom-diatom reactions. We highlight that the quenching of interferences is less efficient than intuitively expected, leading to asymmetries in state-to-state differential cross sections and marked oscillations in J-resolved reaction probabilities as a function of collision energy.

Modulation of Single-Molecule Magnet Properties: a Theoretical Investigation

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In the beginning of the century, the emergence of lanthanide-based systems exhibiting slow relaxation of their magnetization opened a new chapter in the field of molecular magnetism.[1] These so called Single-Molecule Magnets (SMMs) may find many potential applications such as high-density data storage, molecular spintronic or quantum computing.[2] On the computational point of view, the multiconfigurational wavefunction-based SA-CASSCF/RASSI-SO approach is known as a powerful tool to obtain a good description of both the electronic and magnetic features of lanthanide-based SMMs. We will focus on the application of such computational protocol to describe the modulation of the SMM properties observed in two different recently characterized architectures. We will investigate the evolution of the relaxation mechanisms occuring in both an Er(III)-based polyoxometallate and an extended-tetrathiafulvalene Dy(III)-based dimer (Fig. 1) upon hydration/dehydration and reversible redox- and hydro-magnetic switching processes, respectively.

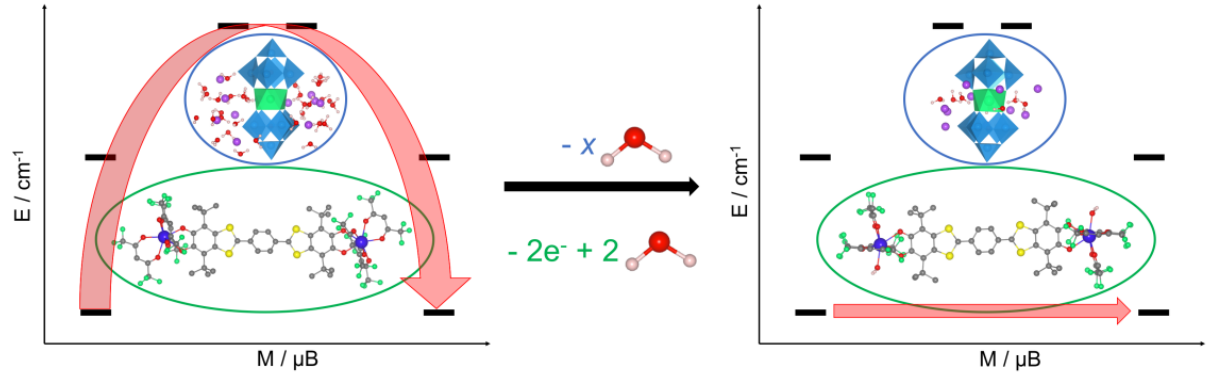

Figure 1 From slow (left) to fast (right) relaxation of the magnetization in Er(III) (blue) and Dy(III) (green) systems

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Dissociating water with inhomogeneous junctions

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Silicon (Si) is one of the most attractive electrode materials for manufacturing photoelectrochemical cells (PECs) because it has a small band gap, it is very abundant and widely used by the photovoltaic industry.[1] Nevertheless, using Si as a photoanode material is highly challenging as oxygen evolution reaction (OER) is sluggish at Si surface and the material is particularly prone to deactivation by spontaneous oxidation and chemical etching. It is known that conformal Ni and NiO_x thin films, deposited by vacuum processes are excellent coating materials, providing corrosion resistance and a high catalytic activity for the OER at high pH.[2]

This poster aims to present our recent works on partially-coated Si photoanodes. Indeed, we have recently shown that transition metals, electrodeposited on *n*-type Si from aqueous solutions, in the form of isolated or coalescent nanoparticles (NPs) protects the underlying and partially exposed Si from photocorrosion under simulated sunlight at pH 14.[3] This is remarkable as most of the surface is not covered, thus, in direct contact with the highly corrosive electrolyte. This phenomenon breaks with the common strategies employed for photoelectrode protection by demonstrating that robust and efficient Si photoanodes can be produced easily, which opens new opportunities for the implementation of low-cost Si-based monolithic photoelectrochemical cells for efficient solar fuel production.[4]

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Blue-Green-Black phosphorene allotropes: A structural and energetic analysis.

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In this study, we try to explain the origin of the phosphorene structure, especially the origin of the rippled one, which is currently the subject of several studies. Phosphorene could exist in different allotropic forms. We have been interested in three allotropic forms namely Blue, Green and Black phosphorene. They are clause of each other as well structurally as energetically but they are different in terms of properties. In fact, the Black one is regarded as a promising material in the electronics industry since it's the unique known, until today, having a sizable fundamental and tunable bond gap and a significant carrier mobility. We will also show that the black phosphorene can undergo an easy conversion to the blue one. This kind of transformation could, among others, confers to him a potential application in the electronics field.

DFT (Density Functional Theory) was used for theoretical calculations employed in our work with the Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation function (B3LYP). The study has been undertaken at high levels of theory like 6-311+G(3df,2p) basis set. NBO (natural bond orbital) computations were utilized to evaluate the effects of hyperconjugative interactions.

Electrochemistry and radiolysis: two aspects of redox reactivity

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In pulse radiolysis, a high energy (about 7 MeV) electron pulse passes through a solution. The loss of energy of the radiation induces breakdown of the solvent and formation of so-called primary species, mainly the solvated electron e^-_{aq} and hydroxyl radical $OH^\bullet$ in water. By adding specific quenchers, it is possible to prepare an oxidative or reductive medium, so that pulse radiolysis has been recognized for long as an interesting method to study homogeneous redox reactions and is very complementary to electrochemistry. Detection is usually performed spectroscopically.

Recently, we established an electrochemical detection of the radiolytic species induced by a picosecond electron pulse, a method pioneered in the seventies by Henglein et al. but then abandoned [1]. The first example will concern reactivity of the guanosine radical. Guanosine is indeed the most sensitive base of DNA towards oxidation. Apart from traditional electrochemical detection, here the radical may be oxidized AND reduced at the working potential. The measured current then results from these two competitive paths. Analysis is performed in the framework of Marcus theory which allows to deduce the reorganization energy of the system but also the redox potential for oxidation the radical [2].

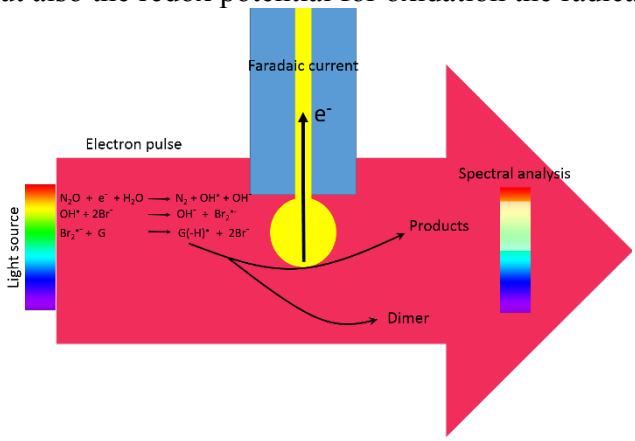

Figure 1 Principe of electrochemical detection of transient species created by pulse radiolysis

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PAHs on/in water ice: structures, energetics and spectra from FTIR experiments and a multi-method theoretical study

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Polycyclic Aromatic Hydrocarbons (PAHs) have been proposed to be the carriers of the Aromatic Interstellar Bands (AIBs), a set of infrared (IR) emission bands observed in the [3 - 15 μm] range in many regions of the interstellar medium (ISM). In dense environments, PAHs are likely to condense onto or integrate into water ice mantles covering dust grains and to contribute to the complex grain chemistry [1]. Understanding the role of ice in the processes involving adsorbed PAHs is therefore a key issue in astrochemistry. Our joint theoretical (classical molecular dynamics/force field simulations and SCC-DFTB calculations) and experimental (matrix isolation/solid phase FTIR spectroscopy) study has given rise to several conclusions, namely: the role of water clusters [2] and of the ice structure [3] on the photo-reactions of PAHs with water ice. We will present evidence of how the surface of amorphous solid water (ASW) is perturbed by the adsorption of PAHs [4] and a complete description of PAH-ice interaction in the ground electronic state at low temperature, providing the binding energies and barrier heights necessary to the on-going improvement of astrochemical models [5a]. The influence of ice on the ionization potential (VIP) of PAHs [5b] will be discussed, together with its astrophysical implications.

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On the key role of fluorination and dual hydrogen bonding in the activation of the epoxide/CO_2 coupling by fluorinated alcohols : a DFT study

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The synthesis of five-membered cyclic carbonates *via* the catalytic coupling of CO_2 with epoxides is currently the subject of numerous studies[1,2]. Recently, we reported a novel combination of onium salts with catalytic amount of Hydrogen Bond Donors (HBDs) allowing the fast synthesis of cyclic carbonates within a few minutes under solvent free and mild experimental conditions.[3] In a recent comparative study highlighting the cocatalytic activity of a series of commercially available HBDs, we demonstrated that fluorinated alcohols were the most efficient HBDs for the synthesis of cyclic carbonates from CO_2 and epoxides under mild experimental conditions.[4] This prompt us to understand the origin of the unprecedented catalytic activity of fluorinated alcohol in comparison with other HBDs proposed in the literature. In this study, we report on the detailed mechanistic investigation, thought Density Functional Theory (DFT) of the CO_2/propylene oxide coupling catalyzed by a bicomponent organocatalyst combining the use of TBABr with (multi)phenolic of fluorinated HBDs.
Thus, it was shown that increasing the number of electron withdrawing trifluoromethyl substituents in HBDs strengthens their proton donor capability and allows a better stabilization by hydrogen bonding of the intermediates and transition states. In addition, the high efficiency of fluorinated monoalcohol activators is related to a dual hydrogen bonding mechanism by two fluorinated molecules that cooperatively contribute to the CO_2/propylene oxide coupling.[5]

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Use of Hyphenated Techniques for the study of the active compounds of Corsican liverwort *Scapania undulata*

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S. undulata is a liverwort living wild on the rocks of deciduous broadleaved forests of Corsica. To our knowledge, four studies deals with the chemical composition of *S. undulata* essential oil from Europe. Some sesquiterpenes such as longibornane and himachalane derivatives were identified as main components. The aim of the present work was to determine and characterize the volatile compounds of *S. undulata* from Corsica using hyphenated technics.

Plant material was collected in several Corsican forests and dried at room temperature. Essential oils and hydrosols were prepared by hydrodistillation and the volatile fraction emitted by the plant was extracted by HS-SPME under optimized conditions. Et_2O extract was also prepared by maceration from powdered plant material. The present study focuses on the volatile components of *S. undulata* from Corsica. The plant volatile metabolites were investigated using an analytical procedure including LC, LLE, GC-FID, GC-MS, ESI-MS, tandem MS and NMR.

The chemical investigations of the four extracts allow determining different chemical profiles. Essential oil (EO), hydrosol (HY) and Et_2O extract (EXT) were dominated by oxygenated sesquiterpenes (EO 63.5%; HY 82.0% and EXT 63.9%) while the volatile fraction (VF) sampled by HS-SPME was dominated by hydrocarbon compounds (61.2%). The main components of essential oil and hydrosol of *S. undulata* were respectively epicubenol (49.0% and 64.5%), τ-muurolol (5.0% and 7.2%) and longiborneol (3.0% and 7.2%) while epicubenol (44.4%) and longipinanol (11.9%) were the main components of Et_2O extract. As previously reported, longipinanol is rather labile and was almost completely degraded during hydrodistillation, but was detected in considerable amounts in the non-aqueous ether extract [3]. In addition, epicubenol (27%), calarene (9.6%), were the main components of the volatile fraction sampled by HS-SMPE. As epicubenol, himachalol, longiborneol and logipinanol were absents to our spectral home-library, their identifications were ensured by NMR and ESI-MS experiments.

The study provides an overview of the volatile components of *S. undulata*. Sesquiterpenes were the dominant natural volatiles of the plant. Oxygenated compounds characterized essential oil, hydrosol and Et_2O extract while hydrocarbons were the predominant volatiles emitted by the plant. The study confirms the necessity to use different sample preparation methods in order to study the complete chemical diversity of the plant.

Analytical investigations of the volatile metabolites extracted from *Xanthium Spinosum* L., an invasive species from Corsica

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In Corsica 53 introduced plant species have been reported and among them 17 were considered as invasives. *X. spinosum* (Spiny coklebur) is a highly invasive plant originated from South America that largely colonized Corsican farmlands where it cause a sanitary risk for cattle [1].

The plant was known for their biological and pharmaceutical activities, imputed to sesquiterpenic lactones called xanthanolides [2]. One of these, Xanthatin exhibited antimicrobial, antifungal activities and anticancer properties [3]. Moreover Xanthatin might be responsible together with two another lactones : loliolide and xanthanol, to the allelopathic effect of *X. spinosum* [4]. Several studies described the chemical composition of the plant extracts, however, to our knowledge, only one work described the chemical composition of the essential oil from aerial parts [5] and the volatile metabolites from the roots were never investigated.

The aims of the present work were to identify the volatile metabolites of four extracts prepared from *X. spinosum* roots and to evaluate their allelopathic activity. Hexanic extract prepared by maceration (HM), microwave assisted extract (MAE), essential oil (EO) and hydrosol (HY) were investigated using GC-FID, GC/MS and NMR. 62 components accounted for 70.8-92.8% of total extract compositions have been identified. The main components were oxygenated sesquiterpenes (39.1-53.2%) and especially three sesquiterpenes lactones -zinolide, dehydroziniolide and 11-*β*-dehydroziniolide- which the identifications required the implementation of an analytical strategy involved successive chromatography, comprehensive analytical techniques and NMR. Our results deal with the first report of the ^{13}C-NMR data of dehydroziniolide and the occurrence of 11-*β*-dehydroziniolide as natural product.

The allelopathic effects (AE) of EO, HY and a lactone-rich fraction were evaluated on leeks. All extracts inhibited the germination of seeds and the phytotoxicity of the root metabolites of *X. spinosum* was confirmed. The sesquiterpene lactones do not seem to be the only ones responsible to the allelopathic activity, synergetic phenomena with other natural components could be occur.

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La chromatographie gazeuse bidimenionnelle intégrale: un outil d'analyse d'échantillons complexes

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L'analyse d'échantillons complexes contenant des composés ayant des structures chimiques proches peut mener à des co-élutions ne permettant pas leur séparation. Cela empêche leur quantification voire leur identification même en optimisant les paramètres de température, ou la longueur de colonne par exemple [1]. Pour cela, l'ajout d'une seconde colonne, orthogonale à la première (séparation de nature différente), permet d'accroître le facteur de résolution : $R_{tot} = R_1 \times R_2$. La GC bidimensionnelle intégrale (GC×GC) permet de faire passer l'ensemble des fractions de la première à la seconde colonne en piégeant et réinjectant périodiquement les fractions éluées. De nombreux domaines tels que les arômes, parfums, produits pétroliers, ou des disciplines environnementales profitent aujourd'hui de cette technologie. Je présenterai les avancées récentes de notre groupe de recherche sur le développement de protocoles pour la séparation énantiosélective de molécules *via* la GC×GC. Ces protocoles optimisés sont utilisés pour l'analyse de biomolécules chirales telles que les acides aminés et sucres contenues dans des échantillons de météorites [2] ou synthétisées dans les conditions du milieu interstellaire [3,4].

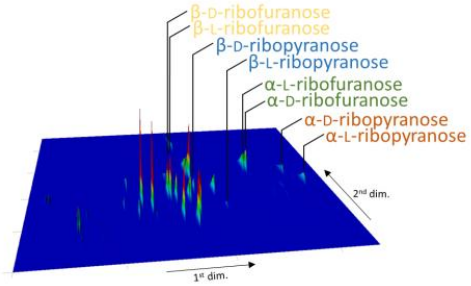

Figure 1 Chromatogramme GC×GC-TOFMS de sucres dérivatisés avec de l'acide trifluoroacétique.

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Investigations of various electroactive films through multi-scale electrogravimetric methods

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Capacitive or faradaic materials are often used as thin films coating the metallic electrode in various applications like energy storage, energy conversion, biosensors domains. Charge transport, charge transfer reactions or electro-adsorption phenomena must play key roles in the electrochemical response of these electroactive films. It is commonly admitted that the oxidation process or anodic potential applied tosuch a film requires either a cation expulsion or an anion entry to compensate for the positive charges formed inside the film. However, it has been shown that these processes in electroactive films are accompanied, not only by the exchange of ions with the electrolyte solution but also by solvent exchanges. As electroneutrality is required, it is generally assumed that the field-assisted transport of charged species is more rapid than the transport of neutral species and, consequently, solvation equilibria can be only slowly established. Therefore, the equilibria associated with electronic, ionic, and solvation processes may be established on quite different time scales, but, at long enough time scales, thermodynamics will prevail and processes will attain a state of global equilibrium. However, the relative rates of all the processes involved in the charge compensation are still an open question.

Different techniques can be used to investigate ionic and solvent transfer and transport in electroactive materials. As the models employed are largely dependent on the techniques used to test them, different approaches can be used. The electrochemical investigation of electroactive films, in terms of voltammetry and electrochemical impedances, takes into account the charged species involved in the electrochemical process of the film. The addition of gravimetric investigations thanks to quartz crystal microbalances allows the solvent interaction to be attained. In order to discriminate the contribution of each involved species, charged or not, a multi scale coupling method of characterization was developed by coupling a fast quartz crystal microbalance to electrochemical impedances measurements. More precisely, ac-electrogravimetry allows the mass response to a small potential perturbation to be analyzed thanks to this fast quartz crystal microbalance used in dynamic regime [1]. Thus, ac-electrogravimetry was employed to characterize ions and solvent motion at the film/electrolyte interface during the electrochemical reactions of electroactive material.

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Hygroscopic Behavior and Chemical Composition Evolution of Aerosols Generated from Mixture Solutions of 3-Methyl-1,2,3-butanetricarboxylic Acid (MBTCA) and NaCl

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Secondary organic aerosols (SOAs), formed and transformed through complex physico-chemical processes in the atmosphere, have received much attention over the past decades due to their impacts on both climate change and human health [1]. The interactions between the organic and inorganic components may alter their hygroscopic properties [2]. Recently, 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a later generation product of the monoterpenes, has been proposed as one of the most relevant tracer compounds for biogenic SOA formation [3], so that MBTCA was selected for this study to improve our knowledge about its properties.

In the present work, laboratory generated, micrometer sized, pure MBTCA and NaCl-MBTCA mixture aerosol particles of four mixing ratios (molar ratios=1:1, 2:1, 3:1, and 1:2), were examined to observe their hygroscopic behavior by varying the relative humidity (RH) and obtain chemical micro-structures using in-situ Raman microspectrometry (RMS) assembled with either a see-through impactor where the particles are deposited on the Si wafer or a levitation system. The pure MBTCA effloresced around 50% and was not dissolved with increasing the RH until 95%. Observation and Raman analysis indicated only mono-sodium tricarboxylate (MSMBTL) can be formed in the mixture. The mixtures under mixing ratios of 1:1 and 1:2 showed no ERH and DRH because of the consumption of the NaCl during reaction in the see-through impactor system, while the mixture under mixing ratio of 1:1 in the levitation system showed a DRH around 71%, suggesting less or no reaction between the two components. The differences might be caused by the system. The other mixtures experienced single-stage efflorescence and deliquescence due to heterogeneous nucleation onto the excess NaCl and the dissolution of the NaCl, respectively. The study revealed that the interactions between the organic and inorganic compositions could modify the SOA properties in the atmosphere as reported before [4]. Further analysis on the reactivity of the MBTCA is under progress for detailed information using RMS.

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Colocalized atomic force microscopy and total internal reflection surface-enhanced Raman scattering spectroscopy method:

Application to the study of the substitution of polyvinylpyrrolidone molecules by 11-mercaptoundecanoic acid on Ag nanowires in an ethanol solution

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An original in-situ total-internal-reflection (TIR) surface-enhanced Raman scattering (SERS) spectroscopic method is described and used to study the substitution of polyvinylpyrrolidone (PVP) molecules on assynthesized PVP-coated Ag nanowires (AgNWs) by their 11-mercaptoundecanoic acid (MUA) counterparts in ethanol solution. The relevance of the SERS approach to examine the anchoring of the MUA onto the silver surface of specific AgNWs with pentagonal cross-sections is supported by FDTD simulations and dark field Rayleigh scattering measurements (DFRSM) [1,2]. The TIR-SERS technique reveals that the PVP-MUA substitution process can be divided into two main steps, namely (i) the desorption of PVP molecules associated with the anchoring of MUA molecules via the formation of Ag-OOC and Ag-S bonds (accomplished within 40 min), and (ii) the subsequent reorientation of MUA molecules to form only Ag-S bonds (finished in 90 min). The resulting passivation of AgNWs of high interest for optoelectronics with MUA significantly improves their resistance to corrosion, which is crucial for future commercial applications [3].

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Pollen diversity and volatile variability of Corsican blossom honey

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The Corsican honey was certified by the european "Protected Designation of Origin (P.D.O): Miel de Corse-Mele di Corsica" and was classified in six varietal categories: "spring", "spring maquis", "honeydew", "summer maquis", "chestnut grove" and "automne maquis". The quality assessment of Corsican honey was essentially based on melissopalynological data taking into account the entire pollen spectrum and completed by physico-chemical parameters [1-3]. The aim of this work was to characterize the volatile composition of Corsica blossom honey and to develop an interdisciplinary approach to complete the characterization of Corsican honey and the qualification of the botanical and/or geographical origin.

In this work, botanical origin of 195 nectar honeys commercialized under P.D.O, were certified by melissopalynological analyses. The volatile composition of samples was established using Headspace-solid phase microextraction (HS-SPME) followed by GC-FID and GC-MS analyses.

Pollen analysis allowed the certification of Corsican origin and highlights the main nectariferous species and/or characteristic plant associations of each varietal range. The analysis of volatile fraction allowed the identification of 80 compounds amounting to 60.7 – 99.7 % of the total composition [4]. The volatile fraction of Corsican honeys was dominated by aromatic compounds (32.9 – 56.4 %), except for "autumn maquis" honeys with isophorone derivatives (42.5 %) as major components class. Otherwise, some chemical markers of botanical origins were identified as 2-aminoacetophenone ("chestnut grove"); *p*-anisaldehyde and 4-n-propylanisole ("spring maquis"); isophorone and 3,4,5-trimethylphenol ("automne maquis"); isomers of lilac aldehydes and *p*-menth-1-en-9-al ("spring clementine") [4]. The "spring non-clementine" and "summer maquis" honeys were both dominated by phenylacetaldehyde and benzaldehyde.

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Dim. 06/10/19		Lun. 07/10/19		Mar. 08/10/19		Mer. 09/10/19	
Accueil des participants		8h45	Introduction	8h45	Introduction	8h45	Introduction
		8h50-9h35	Budzinski	8h50-9h20	Gustavsson	8h50-9h20	Mostafavi
				9h25-9h40	Carayon	9h25-9h40	Lepere
		9h40-9h55	Labat	9h40-9h55	Jegat	9h40-9h55	Abdelmouleb
		10h00-10h15	Mongin	10h00-10h15	Chevalier	10h00-10h15	Alcaraz
		10h15-10h45	Pause				
		10h45-11h20	Simon	10h45-11h00	Calupitan	10h45-11h20	Martzel
				11h00-11h15	Poggi		
		11h20-11h35	Dru	11h15-11h30	Soppera	11h20-11h35	Pineau
		11h35-11h50	Pardanaud	11h30-11h45	McClenaghan	11h35-11h50	Minisalle
		11h50-12h05	Karam	11h45-12h00	Dezalay	11h50-12h05	Houjeij
		12h05-12h20	Guerineau	12h00-12h15	Laurent	12h05-12h20	Baux
						12h20 -12h30	Conclusion
			Déjeuner				
		14h15-14h50	Lojou	14h15-14h50	Alducin		
		14h50-15h05	Lenne	14h50-15h05	Wang Jing		
		15h05-15h20	Loget	15h05-15h20	Bessonne		
		15h20-15h35	Dauphin	15h20-15h35	Donnon		
		15h35-15h50	Alvarez	15h35-15h50	Stirnemann		
		15h50-16h20	Pause				
		16h20-16h55	Alévêque/Levillain	16h20-16h35	Latouche		
				16h35-16h50	Sarr		
		16h55-17h10	Tricoire	16h50-17h05	Michaut		
		17h10-17h25	Simon G.	17h05-17h20	Huart		
18h00-18h15	Introduction	17h25-17h40	Tricard	17h20-17h55	Senjean		
18h20-18h50	Fargette	17h40-17h55	Carn				
19h15 – 20h45	Diner	Session Poster Diner Conseil de la DCP		Social Event + diner de gala			
20h45 – 21h15	Meinert						