Annual NISM meeting 2020

Online conference on Teams
November 20th 2020

Live Teams:

Welcome, Prof. Vincent LIÉGEOIS *9H00-9H10*

Oral session

Invited talk, chairman Prof. Guillaume BERIONNI

Prof. Jean-Marie RAQUEZ	"Design of bioactive composite materials made of bioresorbable poly(L,Llactide): from extrusion to plasma treatments."	*9H10-9H50*

Invited talk, chairman Prof. Yoann OLIVIER

Prof. Daniel Escudero	"Quantitative determinations of photochemistry: are we there yet?"	*9H50-10H30*

Recorded:

Video capsules session *10H30-12H30*

The following papers will be accessible as videos on the conference day (follow the link https://medias.unamur.be/channels/#nism-annual-day-2020)

(Free consultation and Q&A in the corresponding video comments)

Video capsules stay available along the conference day and can therefore be freely viewed but the real-time discussion is only guaranteed during this time slot.

1	Alireza BAGHERPOUR	Hydrogenated amorphous carbon (a-C:H) thin films deposited by low pressure plasma: study of the bias voltage and pressure dependencies of morphology and tensile behavior
2	Quentin BIZOT	Evaluation of materials and cathode shape for an efficient lithium-oxygen battery
3	Florian BOCCHESE	Prediction of thin film composition deposited by magnetron sputtering
4	Laurie BODART	Combining clofazimine and 4-aminosalicylic acid, two antitubercular drugs, to improve clofazimine solubility and 4-aminosalicylic thermal stability
5	Charlotte BOUQUIAUX	Multiscale theoretical investigation of the second harmonic generation of the di-ANEPPS dye in a collection of lipid membranes
6	Roshan CASTELINO	Study of nitrogen doping in single-layer MoTe2 films by RF plasma treatment
7	Tanguy COLLEU-BANSE	Near-field and electrodynamic modes in plasmonic systems
8	Dr. Emile HAYE	Glancing angle deposition of CrN film for supercapacitor application

9	Antoine HONET	Electronic and optical properties of molecules and nanoparticles: the role of electronic correlation
10	Valentin JOB	Study of the antibacterial properties of silver-doped amorphous carbon coatings produced by hybrid PVD/PECVD process
11	Dr. Laura LE BRAS	Paving the way for the computational design of supramolecular drugs
12	Dr. Michael LOBET	Near-zero refractive index photonics and modifications of fundamental radiative processes
13	Damien MAHAUT	9-phosphatriptycenes as Lewis bases in frustrated Lewis pair chemistry: Experimental and quantum chemical approaches
14	Manon MIRGAUX	A structural study by crystallography and Molecular Dynamics of hIDO1 to assist design of original inhibitors
15	Dr. Pavel MOSKOVKIN	Simulation of multi-layer TiN/TiAlN thin film growth and calculation of its thermal conductivity
16	Dr. Jérôme MÛLLER	Multi-scale modelling of SiO2 coating deposited by PECVD
17	Tarcius NASCIMENTO RAMOS	Aggregation effects on nonlinear optical properties of stilbazolium ion pairs
18	Arnaud OSI	From propeller-shaped to non-planar triarylboranes: properties and reactivities
19	Dr. Trung PHAM THANH	Structural and electronic properties of 1H-MoTe2 films grown on graphene by molecular beam epitaxy
20	Alessandra PIRAS	Photodegradation of Rhodamine B dye by Al-doped ZnO nanoparticles
21	Gaetano RICCI	Inverting the Singlet-Triplet Excitation Energy Gap in Triangle-Shaped Molecular Emitters
22	Chen WENZHANG	Synthesis of functionalized copillar[5]arenes and rotaxane as heteromultivalent scaffolds
23	Alexandra YEROMINA	Supported organic semiconductors for visible-light-promoted efficient C-H arylation of different heteroarenes

Live Teams:

Conclusion and Announcement of the 3 best capsules winners *12H40*

Abstract book

1 / 23

Hydrogenated amorphous carbon (a-C:H) thin films deposited by low pressure plasma: study of the bias voltage and pressure dependencies of morphology and tensile behavior

Alireza Bagherpour [a], Marie-Stéphane Colla[b], Paul Baral[b], Michaël Coulombier[b],

Thomas Pardoen[b], Stéphane Lucas[a]

[a] *Laboratoire d'Analyse par Réaction Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium*

[b] *Institute of Mechanics, Materials and Civil Engineering (iMMC), Université catholique de Louvain, av G Lemaître 4, B-1348, Louvain-la-Neuve, Belgium*

Email :alireza.bagherpour@unamur.be

Abstract

In the present work, the mechanical and fracture behavior of thin amorphous carbon films related to deposition conditions were quantitatively characterized by in-situ tensile test and nanoindentation. The amorphous carbon films with different deposition condition (5mtorr, 20mtorr sputtering pressure, floating or 100V bias voltage), were obtained by plasma enhanced vapor deposition with an Ar/C_2H_2 discharge. Columnar shape and small defects on the surface have been observed by SEM. Also, Stoney measurement shows that the films are in large compressive stress (~700 MPa). The results also showed denser film with increasing substrate bias voltage and decreasing pressure, as well as higher toughness and fracture stress. Overally, better mechanical and morphological behavior was observed in high bias and low sputtering pressure.

Evaluation of materials and cathode shape for an efficient lithium-oxygen battery

Quentin BIZOT

Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, Belgium,
E-mail: quentin.bizot@unamur.be

The global need for energy, combined with a desire to be more environmentally friendly, has led to a real increase in electricity consumption, with an average annual increase of 3.4%, 1.2 percentage points higher than average annual growth of energy consumption.[1] As not all the electricity produced can be used immediately, the utilisation of batteries to store unconsumed electricity becomes a key point in these energy issues.

In this optic, lithium-oxygen batteries could be the best candidate, due to their high theoretical energy density which could allow to increase by 15 times the actual storage of lithium-ion batteries (11,680 $W.h.kg^{-1}$).[2,3] Nevertheless, performances of current lithium-oxygen batteries are still quite far from the theoretical values. Indeed, improving electrochemical performances such as rate capability or cycle life are still challenging.[4]

In this talk, I will present the different structures and materials obtained in our laboratory in order to evaluate their performance as cathodes in lithium oxygen batteries. These innovative structures will be multiple, ranging from carbon-based structures with hierarchically ordered porosity following Murray's law allowing optimal diffusion of the electrolyte within the cathode, to carbon slurry containing catalysts based on various metal oxides to enhance OER/ORR processes, or finally, spinel-based nanograss allowing optimized deposition of lithium peroxide during discharge.

[1] Liu.Z, Global Energy Interconnection,**1**, 91-100 (2015)

[2] K. M. Abraham and Z. Jiang, J. Electrochem. Soc, **143**, 1, 1-5 (1996).

[3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon, Nat. Mater, **11**, 19–29 (2012).

[4] P. Tan, H. R. Jiang, X. B. Zhu, L. An, C. Y. Jung, L. Wu, L. Shi, W. Shyy, and T. S. Zhao, Applied Energy, **204**, 780–806 (2017).

Prediction of thin film composition deposited by magnetron sputtering

Florian BOCCHESE[1], Stéphane LUCAS[1]

[1]*Laboratoire d'analyse par reactions nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium*

New technologies developed nowadays require new materials with particular properties. Particularly, the influence of their composition on optoelectronic durability or structural properties is researched [1], [2]. However, final material also depends of the experimental technique of deposition. Among them, magnetron sputtering is very popular because it is scalable for industry and ecological. Nevertheless, simulation is used to improve the prediction ability, allowing a more efficient work, and consequently materials and energy saves. Generally, simulation for magnetron sputtering is divided in three steps; sputtering of the target (SRIM [3] or TRIDYN [4]), transport phase (PIC MC software or SIMTRA [5]) and material growth (NASCAM [6]). This group of simulations are referred as virtual coater.

While sputtering of metallic target does not present any difficulty, the use of target containing at least two elements is a dynamic process due to preferential sputtering leading to local composition variation. As the sputtering yield, as well as energy and angular distributions of the sputtered atoms, is often used as input parameter for the virtual coater, the framework simulation has to be as relevant as possible. Moreover, transport phase simulation taking into account ions is time consuming because Maxwell equation has to be solved for each cell. However, during sputtering process, neutral atoms are principally emitted. Thus, we propose to study virtual coater for neutral atom transport through a gas phase without electrodynamic considerations.

In this work, virtual coater evaluates silver deposition rate. Sputtering yield are simulated by SRIM and TRIDYN software leading to the same feature but with different values. Monte Carlo simulations based on kinetic gases theory are performed in order to describe the transport of neutral atoms through an Ar gas.
In this study, we also use a target with a nominal composition of 95.3 at.% of Zn and 4.7 at.% of Al to simulate the sputtering of a compound target with preferential sputtering. We show local composition has a strong influence on composition ratio of the film.

[1] C. G. Granqvist, "Transparent conductors as solar energy materials : A panoramic review," *Sol. Energy Mater. Sol. Cells*, vol. 91, pp. 1529–1598, 2007.

[2] K. Ellmer and A. Bikowski, "Intrinsic and extrinsic doping of ZnO and ZnO alloys," *J. Phys. D. Appl. Phys.*, vol. 49, 2016.

[3] J. F. Ziegler, "SRIM-2003," vol. 220, pp. 1027–1036, 2004.

[4] W. Möller and W. Eckstein, "Tridyn - a trim simulation code including dynamic composition changes," *Nucl. Inst. Methods Phys. Res. B*, vol. 2, pp. 814–818, 1984.

[5] K. Van Aeken, S. Mahieu, and D. Depla, "The metal flux from a rotating cylindrical magnetron: A Monte Carlo simulation," *J. Phys. D. Appl. Phys.*, vol. 41, no. 20, 2008.

[6] S. Lucas and P. Moskovkin, "Simulation at high temperature of atomic deposition , islands coalescence , Ostwald and inverse Ostwald ripening with a general simple kinetic Monte Carlo code," *Thin Solid Films*, vol. 518, no. 18, pp. 5355–5361, 2010.

Combining clofazimine and 4-aminosalicylic acid, two antitubercular drugs, to improve clofazimine solubility and 4-aminosalicylic thermal stability

Laurie Bodart, Nikolay Tumanov, Johan Wouters

Namur Medicine and Drug Innovation Center - Namur Research Institute for LIfe Science (NAMEDIC-NARILIS), Namur Institute of Structured Matter (NISM), Department of Chemistry, University of Namur (UNamur), 61 Rue de Bruxelles, 5000 Namur, Belgium.

E-mail: laurie.bodart@unamur.be

Tuberculosis is an infectious disease caused by *Mycobacterium tuberculosis* which is still among the top causes of death worldwide[1]. Even if drug susceptible tuberculosis is curable, multidrug resistant (MDR) and extensively drug resistant (XDR) strains of *M. tb* have emerged because of bad compliance or inappropriate use of antitubercular drugs.

In this context, clofazimine (CFZ), has been selected to be part of the shortened Bangladesh regimen against MDR tuberculosis[2]. Clofazimine bioavailability is however limited by its low aqueous solubility.

According to the World Health Organization, 4-aminosalicylic acid (PAS) is classified as a group C drug for the treatment of multidrug resistant tuberculosis[3]. PAS is however known to be unstable and in the solid-state, the crystalline powder can decarboxylate under exposition to moisture or heat[4], [5].

The association of CFZ and PAS is reported for the treatment of XDR-TB[6] Zhang *et al.*[7] have further shown that PAS enhanced CFZ activity *in vitro* and Lu *et al.*[8] have even shown a synergistic effect between both drugs. An alternative formulation consisting of salts combining CFZ with PAS could potentially improve clofazimine solubility and PAS stability. The present study reports on the preparation of $CFZNH^+$-PAS^- salts that were characterized in terms of thermal stability and aqueous solubility.

[1] World Health Organization, “Global Tuberculosis Report 2019,” Geneva, Switzerland, 2019.

[2] C. Lange, D. Chesov, and J. Heyckendorf, *Clin. Microbiol. Infect.*, **25**, 128–130, (2019).

[3] World Health Organization, “WHO consolidated guidelines on drug-resistant tuberculosis treatment,” 2019.

[4] S. S. Kornblum and B. J. Sciarrone, *J. Pharm. Sci.*, **53**, 935–941, (1964).

[5] M. Rotich, B. Glass, and M. Brown, *J. Therm. Anal. Calorim.*, **64**, 681–688, (2001).

[6] World Health Organization, *Companion handbook to the WHO guidelines for the programmatic management of drug-resistant tuberculosis*. World Health Organization, 2014.

[7] S. Zhang, W. Shi, J. Feng, W. Zhang, and Y. Zhang, *Emerg. Microbes Infect.*, **6**, e28, (2017).

[8] Y. Lu *et al.*, *Chinese J. Tuberc. Respir. Dis.*, **33**, 675–678, (2010).

Multiscale theoretical investigation of the second harmonic generation of the di-ANEPPS dye in a collection of lipid membranes

Charlotte BOUQUIAUX, Benoît CHAMPAGNE

University of Namur, Theoretical Chemistry Lab, Unit of Theoretical and Structural Physical Chemistry, Namur Institute of Structured Matter, rue de Bruxelles, 61, B-5000 Namur

E-mail: charlotte.bouquiaux@unamur.be

Most biomolecules possess few natural moieties with exploitable optical properties. The use of exogenous dyes can improve the contrast in tissues for being detected by commercially available microscopes. Usually, ANEP-like fluorescent dyes are used, but in the last few years, these compounds have also gained interest in the field of Second Harmonic Generation (SHG). This technique possesses the advantage, with respect to fluorescence, that only non-centrosymmetric region produces a SHG signal.

On this basis, the objective of this work is the elaboration of a multiscale theoretical chemistry method to predict and interpret the SHG responses of dyed lipid membranes and applying it to a hierarchy of lipid membranes of increasing complexity.

Previous work[1] highlighted the huge surrounding effects when considering the influence of the environment on the SHG response of the di-8-ANEPPS (Figure 1) dye [from the isolated gas phase to the 16:0-16:0 PC (phosphatidylcholine) bilayer]. This called for further investigation of the role of the nature of the lipid bilayer on the di-8-ANEPPS SHG properties. In this work, the di-8-ANEPPS NLOphore is embedded in a collection of model lipid membranes. They are composed of: (i) lipids of the same category as 16:0-16:0 PC (zwitterionic glycerophospholipid), 16:0-18:1 PC, and 16:1-16:1 phosphoethanolamine (PE) to study the effect of the unsaturation(s) of the alkyl chains and of the nature of the polar head; (ii) another type of lipid, sphingomyelin (SM); and 18:1-16:0 SM, (iii) various concentrations of cholesterol in 16:0-16:0 PC membranes to obtain the first mixed systems of this study. The systems are currently being modeled via MD simulations, before being validated by comparing structural parameters with experimental data. This poster presents preliminary results of the NLO response of the dye from extracted snapshots and compares the results from one environment to the next.

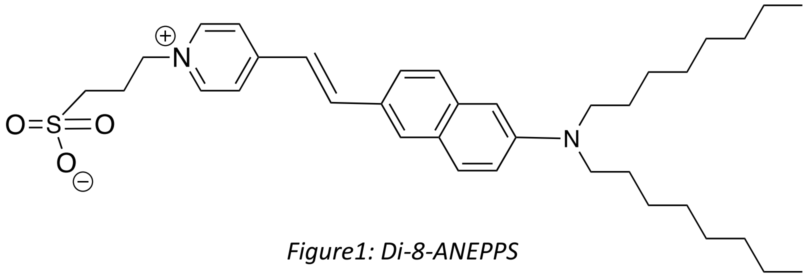


Figure1: Di-8-ANEPPS

[1] Bouquiaux, C.; Tonnelé, C.; Castet, F.; Champagne, B. J. *Phys. Chem. B*, **124**, 2101−2109 (2020).

Study of nitrogen doping in single-layer MoTe₂ films by RF plasma treatment

Roshan CASTELINO[a], Trung T. PHAM[a], Alex FELTEN[b], Robert SPORKEN[a]

[a]***Namur Institute of Structured Matter (NISM),***
[b]***Technological Platform Synthesis, Irradiation and Analysis of Materials (SIAM), Department of Physics, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium***

E-mail: roshan.castelino@unamur.be

Two-dimensional transition metal dichalcogenides (TMDs) are an emerging class of materials that have received wide spread research attentionin recent years.[1] These layered materials are very rich from the electronic standpoint since these can be semiconductors, metals and superconductors. In particular, TMD semiconductors are widely researched for future applications.

Among all the TMD semiconductors, 2*H*-$MoTe_2$ is one of the semiconducting TMDs with the smallest bandgap.[2] Single layer films and those that are a few atomic layers thick have a direct bandgap close to 1 eV, similar to the width of the indirect bandgap of Si, making it attractive not only for controllable ambipolar field-effect transistors (FETs) but also for optoelectronic devices.[3] Therefore, it is highly desirable to grow large-area and uniform mono-/double-layer 2*H*-$MoTe_2$ films for device fabrication. In this context, large area and high crystalline quality of $MoTe_2$ films synthesized by Pham et al.,[4] seem promising for further research. However, in order to expand the scope of their applications, $MoTe_2$ semiconductors need to be doped to higher carrier concentrations. Indeed, DFT calculations on TMDs doped with a non-metal element such as nitrogen have shown significant modification of their surface structure and changes in the electronic properties.[5] Experimental work with nitrogen doped $MoSe_2$ and MoS_2 have confirmed the substitution of chalcogen with nitrogen atoms leading to p-type behaviour[6,7]whereas no such data is available with regard to $MoTe_2$.

In this work, we use molecular beam epitaxy (MBE) to synthesize single/double layer semiconducting $MoTe_2$ on graphene and then, dope it with nitrogen atoms using a remote plasma source. The undoped and doped samples are analyzed by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM). From the XPS and STM analyses, we can confirm modifications of the surface structure by nitrogen. UPS spectra suggest that nitrogen doping of $MoTe_2$ induces a n-type conduction as revealed by the shifting of its valence band~~s~~ to higher binding energies.

[1] Wang, Y. H.; Huang, K. J.; and Wu, X. *Biosensors and Bioelectronics*, **97**, 305-316(2017).
[2] Li, Y.; Zhang, J.; Huang, D.; Sun, H .; Fan, F.; Feng, J .; Wang, Z.; and Ning, C.Z. *Nat. Nanotechnol*, **12**, 987 (2017)
[3] Bie Y.; Grosso G.; Heuck M.; Furchi, M.M.; Cao, Y.; Zheng, J.; Bunandar, D.; Navarro-Moratalla, E.; Zhou, L.; Efetov, D.K.; Taniguchi, T.; Watanabe, K.; Kong, J.; Englund, D.; Jarillo-Herrero, P.; Nat. Nanotechnol, 12, 1124 (2017).
[4] Pham, T.T.; Castelino, R.;Felten, A.; and Sporken, R. *Applied Surface Science*, **146428** (2020).
[5] Singh, Y.; Back, S.;and Jung, Y *ChemElectroChem*, **5**, 24, 4029-4035(2018).
[6] Xia, Y.; Wang, B.; Zhang, J.; Feng, Y.; Li, B.; Ren, X.;and Liu, C. *2D Materials,* **5**, 4, 041005(2018).
[7] Azcatl, A.; Qin, X.; Prakash, A.; Zhang, C.; Cheng, L.; Wang, Q.; and Addou, R. *Nano letters*, **16**, 9, 5437-5443(2016).

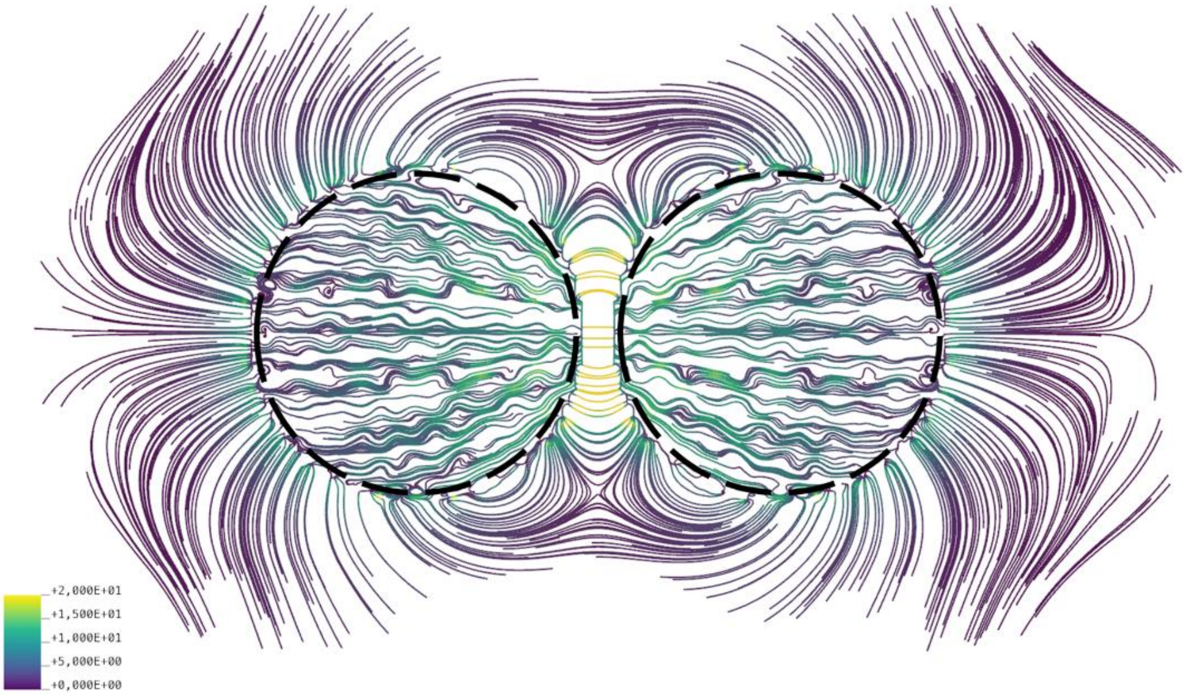
Near-field and electrodynamic modes in plasmonic systems

Tanguy Colleu-Banse[1], Vincent Liégeois[2], Luc Henrard[1],

Laboratoire de Physique du Solide (LPS), Department of Physics[1],
Laboratory of theoretical Chemistry (LTC), Department of Chemistry [2],
University of Namur, Namur
E-mail: tanguy.colleubanse@unamur.be

The SURFASCOPE project aims to simulate Surface Enhanced Raman Spectroscopy (SERS). The very high cross section of the Raman process in SERS relies on the intensity and spatial variation of the near-field response at the position of the probed molecules. In this context, we have simulated plasmonic systems with Discrete-Dipole Approximation. This flash presentation will show the electromagnetic response of several plasmonic devices with a focus on the differences between the far-field response and the near-field response.

The studied particles are a disk, two disks close to each other and a donut-like shape (hollow disk). With those examples, we exemplify the difference between the far-field (scattering cross-section), the near-field inside the particles (absorption cross-section) and the near-field outside the particles (related to the SERS enhancement). The figure below shows the electric field around two disks of gold with a diameter of 10 nm at a plasmonic resonance.



Glancing angle deposition of CrN film for supercapacitor application

Emile HAYE[1], Amine ACHOUR[2], Abdelouadoud GUERRA[3,4], Fatsah MOULAI[3], Toufik HADJERSI[3], Rabah BOUKHERROUB[4], Adriano PANEPINTO[5], Thierry BROUSSE[6,7], Jean-Jacques PIREAUX[2], Stéphane LUCAS[1]

[1] *Laboratoire d'Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium.*
[2] *Laboratoire Interdisciplinaire de Spectroscopie Electronique (LISE), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium.*
[3] *Centre de Recherche en Technologie des Semi-conducteurs pour L'Energétique (CRTSE), Division TESE, 2 Bd. Frantz Fanon, B.P. 140 Alger-7 Merveilles, Alger, Algeria.*
[4] *Univ. Lille, CNRS, Central Lille, ISEN, Univ. Valenciennes, UMR 8520, IEMN, F-59000 Lille, France*
[5] *Chimie des Interactions Plasma-Surface (ChIPS), Université de Mons, 23 Place du Parc, 7000 Mons, Belgium.*
[6] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP32229, 44322, Nantes Cedex 3, France*
[7] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS, 3459, France*
[8] *Université Ferhat Abbas Sétif -1-, El Bez sétif 19000, Algérie.*

The specific capacitance of electrochemical capacitors (ECs) directly depends on the porous morphology of the active area. The control of the surface area is thus a key parameter to control the electrolyte accessibility to the surface of the active material, in order to increase the charge storage. In this view, we demonstrate that the glancing angle deposition (GLAD) magnetron sputtering offers a useful way to deposit active CrN film onto Si electrodes, with controlled surface morphology, due to the shadowing effect of the tilted growing films. In the present work, we investigate the synthesis and the properties of CrN films with variable tilts deposition (0°, 45°, 60 and 75°). The capacitive behaviour of the film appears to be directly dependent on the deposition angle. While the films deposited at 0 and 75° do not present a capacitive behaviour in 0.5 M H_2SO_4 electrolyte, a high areal capacitance of 70.0 mF.cm^{-2} at 1 mA.cm^{-2} is measured for 45 and 60°. Moreover, the films exhibit a good stability, with 85% of retention after 15000 charge/discharge cycles. In addition, on silicon chip interdigitated micro-supercapacitors based on symmetric CrN film (CrN 60°) with a high energy density has been achieved. The GLAD strategy, which is simple and consists of one step process, can be generalised for other types of materials deposited by physical vapour deposition techniques, in order to elaborate highly porous electrodes, with improved electrochemical energy storage properties.

Keywords: CrN; Transition metal nitrides; Electrochemical capacitors; Film porosity; GLAD.

Electronic and optical properties of molecules and nanoparticles : the role of electronic correlation

Antoine HONET[1], Luc HENRARD[1], Vincent MEUNIER[2]

[1]*Department of Physics and NISM, University of Namur, Namur, Belgium*
[2]*Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic*

The optical response of molecules and nanoparticles is at the origin of many static and dynamical properties of matter. As an example, electrochromism is directly related to the modification of the optical absorption with the charge (number of electrons) of the systems.

The modelization and the simulation of such an effect relies of an accurate description of the electronic correlation. In brief, this electron correlation can be defined as the missing part in an independent electron (or mean field) description and is particularly important in collective excitations, such as plasmons.

Tight-binding (TB) is an often-used method to compute electronic properties of molecules and solids systems in the independent electrons picture. It is less frequently used to compute optical absorption of an incident electromagnetic radiation because of the time needed to calculate the atomic polarizability [1, 2].

A way to overcome this limitation is to work in Fourier space [3] which can be also formulated in a Green's function formalism [4]. We then developed the Green's function method to access the polarizability more easily. This formalism applies for TB as well as for a mean field treatment of a Hubbard Hamiltonian, a model that takes into account the electron correlation.

We have developed a self-consistent algorithm that takes into account the electron-electron correlation that is not included in tight-binding or in mean field Hubbard by a so-called GW correction. The reason to use GW correction is to include correlation effects at a small computation cost, in comparison with exact diagonalization.

These developed techniques are now being used to describe PAH and nano-graphene, including electron-doped or nitrogen-doped nano-graphene in order to explore the effect of the dopants and of the correlation between electrons.

[1] Delerue, C. and Lannoo, M. *Nanostructures: Theory and Modeling;* Springer 2004.
[2] Delerue, C. *Nano Lett.* **17**, 7599 (2017).
[3] Thongrattanasiri, S. ; Manjavacas, A. and Javier García de Abajo, F. *ACS Nano* **6**, 1766 (2012).
[4] Joost, J.-P.; Jauho, A.-P. and Bonitz, M. *Nano Lett.* **19**, 9045 (2019).

Study of the antibacterial properties of silver-doped amorphous carbon coatings produced by hybrid PVD/PECVD process

Valentin Job[1], Julie Laloy[2], Jean-Michel Dogné[2] & Stéphane Lucas[1]

[1]Laboratoire d'Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), Department of Physics, University of Namur – 61 Rue de Bruxelles, 5000 Namur, Belgium

[2]Department of Pharmacy, University of Namur – 61 Rue de Bruxelles, 5000 Namur, Belgium

E-mail: valentin.job@unamur.be

Hospital-acquired infections are responsible for a significant part of morbidity and mortality. Approximately 1 in 20 hospitalized patients will acquire an infection that will manifest about 48 hours after admission. A significant part of these infections are due to bacterial pathogens. The chance of contracting such infection for a patient being admitted to an intensive care unit is of about 11 %, and contaminated areas can increase the risk by almost 10 percent.

In this work, we evaluate the possibility to produce and caracterize antibacterial surface.

It aims to optimise a coating made of amorphous carbon matrix doped with silver (a-C:H:Ag) and to evaluate its antibacterial activity. Coatings are produced by a hybrid PVD/PECVD process. The colony-forming unit (CFU), live/dead bacterial viability and Kirby-Bauer diffusion assays were used to assess the toxicity of this coating against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) bacteria. The coatings main features were characterized by X-Ray Photoelectron Spectrometry (XPS) and Scanning Electron Microscopy (SEM). The results obtained during this work shows very promising anti-bacterial activities against the two types of bacteria.

Keywords: antibacterial coating, a-C:H, silver incorporation, S. aureus, E. coli.

Paving the way for the computational design of supramolecular drugs

Laura LE BRAS[a], Yves DORY[b], Benoît CHAMPAGNE[a]

[a] Laboratoire de Chimie Théorique, Namur Institute of Structured Matter (NISM), Université de Namur – Namur, Belgium

[b] Laboratoire de Synthèse Supramoléculaire, Institut de Pharmacologie, Université de Sherbrooke – Sherbrooke, Canada

E-mail: laura.lebras@unamur.be

It has been established that the Parkinson's disease (PD) finds its origin in the aggregative behavior of the α-synuclein (**α-SYN**) protein[1-3]. The aggregates formed are characterized by a stacking of the proteins and a dimerization of those stackings (Figure 1)[4]. Considering and understanding the aggregation process of **α-SYN** thus appears to be a pre-requisite for the development of a drug. One of the strategies to treat PD could be to avoid the formation of the aggregates. It can be achieved through the design of small organic molecules, that will be able to (1) self-assemble as organic nanotubes (**ON**) *via* hydrogen bond network and (2) interact with the large supramolecular assembly that is **α-SYN**. In this sense, the *in silico* design and thus computational chemistry, is a valuable tool. Thanks to a multi-scale approach, combining classical molecular dynamics simulations and quantum chemistry calculations, it will be possible to fully characterize the **ON**. In particular we will be able to provide answers to some fundamental questions such as: Are the identified molecules forming **ONs**? Are **ONs** stable enough? Are they interacting with **α-SYN**? A schematic representation of the concept of the project is provided in Figure 1.

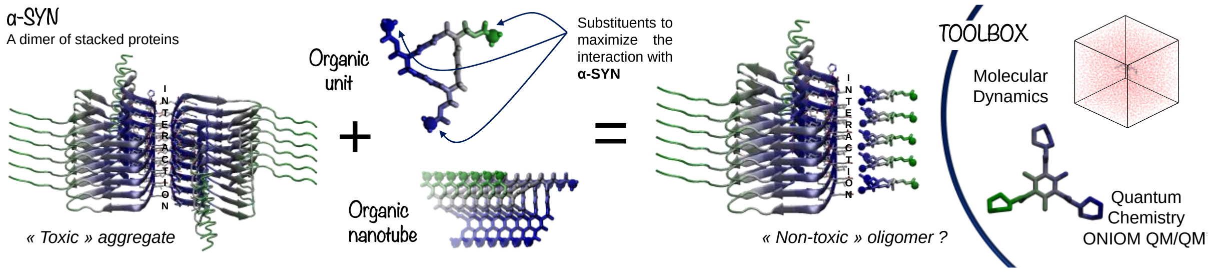


Figure 1. Schematic representation of the concept of the project.

In this presentation we will develop the computational approach and the strategy that has been designed to take into account the large assemblies that are involved (**α-SYN** and **ON**). Then, different families of organic molecules will be considered and their properties as **ON,** as long as their interactions with **α-SYN,** will be investigated.

[1] Soto, C. *Nat Rev Neurosci* **4,** 49 (2003)
[2] Knowles, T. P. J.; Vendruscolo, M.; Dobson, C. M. *Nat Rev Mol Cell Biol* **15,** 384 (2014)
[3] Eisenberg, D.; Jucker, M. *Cell* **148,** 1188 (2012)
[4] Rodriguez, J.; Ivanova, M.; Sawaya, M. *et al.* *Nature* **525,** 486–490 (2015)

Near-zero refractive index photonics and modifications of fundamental radiative processes

M. Lobet

Near-zero refractive index photonics refers to the study of light–matter interactions in the presence of materials/ artificial structures in which one or more of the constitutive parameters are near-zero. It can be either the relative permittivity or the relative permeability or both. Consequently, a decoupling of electricity and magnetism is present, the wavelength is stretched, the phase distribution of electric and magnetic field is nearly constant and the phase velocity is infinite.

We will first review the unique features that differentiate near-zero refractive index materials from other structured materials.

Then we present our last results on modification of the three fundamental radiative processes that describes light-matter interactions (absorption, spontaneous emission and stimulated emission within media with a vanishingly small refractive index. A generalized framework is derived in order to capture the effect of the spatial dimension of the NZI medium on the nature of the fundamental radiative processes. Our formalism also analyses the role of the number of available optical modes and the ability of an emitter to couple to these modes as a function of both the class and the dimension of the NZI material. As a result, spontaneous emission is inhibited in 3D homogeneous lossless zero index media but can be enhanced in a NZI material of reduced dimensionality.

References:

I. Liberal, N. Engheta, "Near-zero refractive index photonics", Nature Photon 11, 149–158 (2017)
M. Lobet, I. Liberal, E. N. Knall, M. Zahirul Alam, O. Reshef, R. W. Boyd, N. Engheta, E. Mazur, "Fundamental Radiative Processes in Near-Zero-Index Media of Various Dimensionalities", ACS Photonics, 7 (8), 1965-1970 (2020).

13 / 23

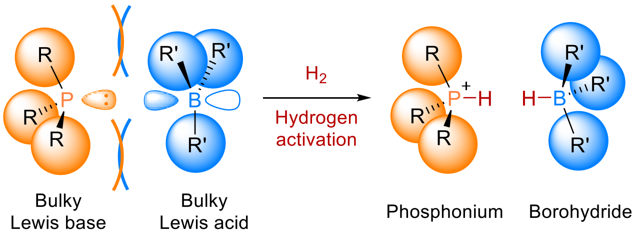
9-phosphatriptycenes as Lewis bases in frustrated Lewis pair chemistry: Experimental and quantum chemical approaches

[1,2]Damien MAHAUT, [1]Lei HU, [2]Benoît CHAMPAGNE, [1]Guillaume BERIONNI

[1] Laboratoire de Réactivité et Catalyse Organique ; [2] Laboratoire de Chimie Théorique,
Department of Chemistry, Namur Institute of Structured Matter,
University of Namur - Rue de Bruxelles 61, B-5000 Namur, Belgium

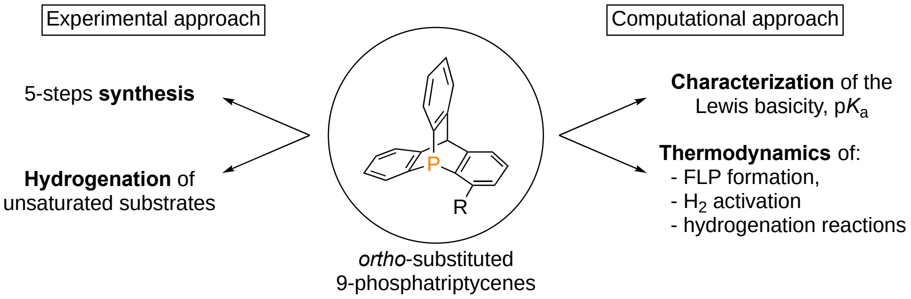
E-mail: guillaume.berionni@unamur.be, benoit.champagne@unamur.be

Frustrated Lewis Pairs (FLPs) consist in sterically hindered Lewis acids and bases which cannot form Lewis adducts because of steric repulsions. These bifunctional systems have been extensively used as transition metal-free catalysts for hydrogenation reactions and small molecules activation (CO_2, NO_2, …).[1,2]



The synthesis of new sterically hindered Lewis bases is crucial for the development of new types of FLP catalysts. Due to their cage-like structure, 9-phosphatriptycene derivatives constitute promising Lewis bases in this context. For example, the enhanced pyramidalization of the phosphorus results in a weakening of its Lewis basicity and an increased steric bulk compared to related triarylphosphines.[3]

This flash presentation will summarize our experimental and computational investigations on 9-phosphatriptycenes in FLP chemistry. Our synthetic strategy to obtain bulky *ortho*-substituted phosphatriptycenes is based on the use of *ortho*-functionalized triarylphosphine or triarylmethane precursors. In addition, a density functional theory study of the structural and electronic parameters of these compounds as well as their thermodynamics in FLP chemistry for H_2 activation and hydrogenation reactions will be presented.



[1] D. W. Stephan, *Science*, **2016**, *354*, 1248.
[2] J. Lam, K. M. Szkop, E. Mosaferi, D. W. Stephan, *Chem. Soc. Rev.*, **2019**, *48*, 3592.
[3] L. Hu, D. Mahaut, N. Tumanov, J. Wouters, R. Robiette, G. Berionni, *J. Org. Chem.*, **2019**, *84*, 11268.

A structural study by crystallography and Molecular Dynamics of hIDO1 to assist design of original inhibitors

[1]Manon Mirgaux, [1]Laurence Leherte, [1]Johan Wouters

[1] Laboratoire de Chimie Biologique Structurale (CBS), Namur Institute of Structural Matter (NISM), Namur Research Institute for Life Sciences (NARILIS), University of Namur (UNamur), Belgium, Email: manon.mirgaux@unamur.be.

Due to its degradation into numerous bioactive metabolites, L-Tryptophan (L-Trp) is the less abundant but essential amino acid in mammals. [1] The main way to transform L-Trp is the kynurenine pathway (KP, **Figure 1**), allowing the transformation of 95\% of the L-Tryptophan available from food. [2] Through KP, L-Trp is converted into L-kynurenine to produce essential metabolites such as redox cofactors, neuroprotectors and neurotoxics. [3] As a result, the KP pathway confers to L-Trp a central role in many diseases. [2, 4] Therefore, enzymes of the kynurenine pathway can be considered as a set of therapeutic targets. Particularly, the first step of this road, catalyzed by hIDO1 or hTDO, raised an interest in the cancer research in cancer immune escape and in the resistance to immunotherapy. [5] Over the years, hIDO1 inhibitors have been developed (Indoximod, Epacadostat, PF-06844003, Navoximod and Linrodostat) but, recently, the most advanced of them (Epacadostat) failed in the clinical trial. [6]

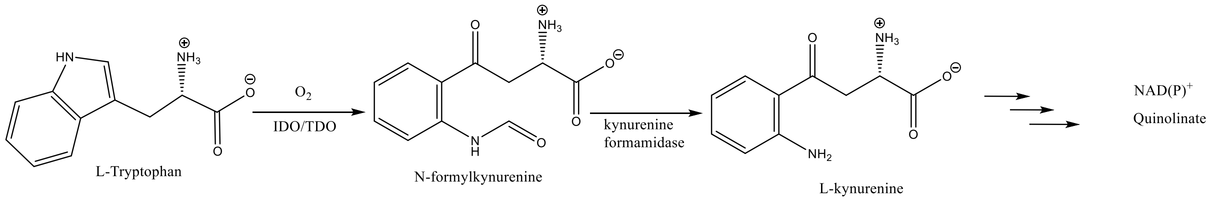


Figure 2 - Kynurenine pathway : hIDO and hTDO regulate the first step.

Since 2006, several structures of hIDO1 are deposited on the PDB. However, a loop of the enzyme, the JK-loop, has never been resolved. As the JK-loop is very likely involved in the closure of the active site, this loop plays a key role in the mechanism and the inhibition. [7] Recent fails in clinical trials of hIDO1 inhibitors trigger a revision of the enzyme functioning involving the JK-loop. [6] It is recognized that there is a lack of structural information on hIDO1 to understand the key role of the JK-loop.

In the present work, the refinement of the JK-loop is obtained for the first time by X-ray diffraction experiment, thanks to its crystal packing mode. To support the X-ray observation, Molecular Dynamics trajectories are also carried out to provide a dynamical information about the loop in the presence of the cofactor. Such new structural and dynamical information highlights the importance of the JK-loop in confining the labile heme cofactor into the active site.

[1] A. Badawy. International Journal of Tryptophan Research, 10, 2017.
[2] R. S. Phillips et al. Frontiers in molecular biosciences, 6, 2019.
[3] L. R. Kolodziej. Amino acids, 41:1173–1183, 2011.
[4] A. L. Mellor et al. Frontiers in immunology, 8:1360, 2017.
[5] C. Uyttenhove et al. Nature medicine, 9(10):1269–1274, 2003.
[6] G. V. Long et al. The Lancet Oncology, 20(8):1083–1097, 2019.
[7] L. Álvarez et al. Biochemistry, 55(19):2785–2793, 2016.

Simulation of multi-layer TiN/TiAlN thin film growth and calculation of its thermal conductivity

P. Moskovkin(1), J. Müller(1) and S. Lucas(1)

(1) University of Namur (PMR-LARN-NISM), rue de Bruxelles 61, B-5000 Namur, Belgium)
E-mail: pavel.moskovkim@unamur.be

Multi-layer titanium nitride/titanium aluminium nitride film growth was simulated by means of kinetic Monte Carlo code NASCAM [1]. Results of the simulation were compared to experimental data [2]. Film growth was simulated for different number of bi-layers TiN/TiAlN, with the number of bi-layers equals from 5 to 50. The total thickness of the whole stack was the same for all samples. That means that the thickness of bi-layers became smaller with the increase of bi-layer numbers.

Calculation of the thermal conductivity of simulated multi-layer film was conducted in two steps. Firstly, the thermal conductivity of the single layer was calculated by using Landauer relation based on effective medium theory [3]. Secondly, the thermal conductivity of the whole stack was calculated the following equation:

$$\frac{1}{k} = \sum_{i=1}^{N} \frac{l_i/l}{k_i} + \sum_{j=1}^{N-1} r_j,$$

where k_i is a thermal conductivity of a sub-layer *"i"* , l_i is a thickness of the sub-layer *"i"*, l is the total thickness of the layer, and *N* is the number of sub-layers and r_j are thermal resistivities of the interfaces between each TiN and TiAlN layers.

Simulation results were compared to the experimental data and to the results of the calculation by means of the equation given above and it was found the perfect agreement between all the data.

[1] https://www.unamur.be/sciences/physique/ur/larn/logiciels/nascam

[2] M.K. Samani et al, Thermal conductivity of titanium nitride/titanium aluminum nitride multilayer coatings deposited by lateral rotating cathode arc, Thin Solid Films 578 (2015) 133–138).

[3] R. Landauer, The electrical resistance of binary metallic mixtures, J. Appl. Phys. 23, 779-784, 1952

Multi-scale modelling of SiO2 coating deposited by PECVD

J. Müller[(1)], P. Moskovkin[(1)] and S. Lucas[(1)]

(1) University of Namur (PMR-LARN-NISM), rue de Bruxelles 61, B-5000 Namur, Belgium)
E-mail: jerome.muller@unamur.be

SiO2 layers produced by PECVD (Plasma Enhanced Chemical Vapor Deposition) can be used as protective layers (corrosion, anti-scratch), barrier layers (dielectric, moisture), easy-to-clean coatings based on hydrophilicity, adhesion promoter. In addition, SiO2 is the one of the most used low refractive index material in optical applications. In combination with complementary high-index thin films such as TiO2, it can be used to enhance light reflectance in reflector systems, or solar absorbance. Consequently, SiO2 layers are found in numerous applications, including packaging, automotive, optical components, building industries... Then, modelling such deposition process is a substantial step to improve plasma assisted deposition techniques at SMEs and industries.

This task aims for developing a realistic process model for SiO2 deposition via a capacitive coupled PECVD source with HMDSO as main precursor and O2 as reactive gas. Deposition mechanisms in PECVD involve the excitation and/or ionization of gas molecules in the region of dense plasma thereby generating radicals. Depending on the gas flow dynamics, the radicals and reactive gas are transported towards the substrate where the film growth is highly impacted by surface chemical reactions. However, the plasma discharge, the gas transport and film growth act on vastly different timescales. It is therefore not feasible in terms of complexity and computational demands to describe the full process including all possible reaction mechanisms in a single simulation model. Instead, we developed a simplified model taking into account only the most relevant mechanisms for radical formation, and describing the film growth in a kinetic gas flow simulation model which considers the gas transport of radicals and reactive gas (using DSMC method) and the reactive interaction on the film surface (using the advanced version of NASCAM[1]). The development of this simplified PECVD process model was closely coupled with experimental investigations.

[1] https://www.unamur.be/sciences/physique/ur/larn/logiciels/nascam

Aggregation effects on nonlinear optical properties of stilbazolium ion pairs

Tárcius N. Ramos, Benoît Champagne

Theoretical Chemistry Lab, Namur Institute of Structured Matter, University of Namur, rue de Bruxelles, 61, B-5000 Namur, Belgium

E-mail: tarcius.nascimento@unamur.be

The electric field induced second harmonic generation (EFISHG) technique has been widely explored to understand the nonlinear optical (NLO) responses in liquid environments. One requirement for such measurements is the charge neutrality of the targeted compounds, leading therefore to additional challenges on neutral ionic pair complexes. Besides, a wide range of NLO responses values is expected when these ionic compounds aggregate or dissociate. The EFISHG response on ionic pair was firstly measured for amphiphilic polyenic push-pull[1] and recently for pH-triggered NLO switches.[2] Moreover, large concentration dependence on the NLO responses was observed for stilbazolium ion pair derivatives.[3] Theoretical investigations can be used to rationalize these results. However, this requires a multiscale computational approach, where the thermodynamics is included by using molecular dynamics with classical force fields while the electronic structure is accounted for by quantum chemistry methods on selected snapshots. Due to the large computational needs and the complexity of the approach, few theoretical studies have been done to understand this phenomenon.[4,5]

Following the investigation of stilbazolium ion pairs,[3] we have theoretically shown that the relative position between the cation and anion plays a crucial role in tuning the EFISHG response on monomer complexes.[5] Now, we are expanding such studies on dimer aggregates to better understand their large concentration dependence. Our results indicate several aggregation structures since stacked or head-to-head structures change the symmetry of the complexes. In comparison to the values obtained on monomer complexes, the second-order EFISHG contribution ($\mu\beta_{//}$) is reduced by ~50% in dimers due to reductions of μ and $\beta_{//}$ around 70%. On the other hand, the third-order EFISHG contribution ($\gamma_{//}$) is not strongly impacted by the aggregation. One of the studied complexes showed predominantly aggregates in stacked structures. For this case, the value of the $\mu\beta_{//}$ response is ~90% and of the $\gamma_{//}$ is ~70% of the values obtained for monomers. Correlation analyzes indicate that the intermolecular interactions, represented by the relative distances among the ionic species, play a central role in changing the β tensor elements values contrary to the bond length alternation and intramolecular torsion angles.

[1] Alain, V.; Blanchard-Desce, M.; Ledoux-Rak, I.; Zyss, J. *Chem. Commun.* **6,** 353–354 (2000).

[2] Cariati, E.; Dragonetti, C.; Lucenti, E.; Nisic, F.; Righetto, S.; Roberto, D.; Tordin, E. *Chem. Commun.* ***50***, 1608–1610 (2014).

[3] Tessore, F.; Cariati, E.; Cariati, F.; Roberto, D.; Ugo, R.; Mussini, P.; Zuccaccia, C.; Macchioni, A. *ChemPhysChem* **11,** 495–507 (2010).

[4] Pielak, K.; Tonnelé, C.; Sanguinet, L.; Cariati, E.; Righetto, S.; Muccioli, L.; Castet, F.; Champagne, B. *J. Phys. Chem. C* ***122***, 26160–26168 (2018).

[5] Ramos, T. N.; Canuto, S.; Champagne, B. *J. Chem. Inf. Model.* (in press), (2020)

From propeller-shaped to non-planar triarylboranes: properties and reactivities

Arnaud OSI

Reactivité et catalyse organique (RCO), Department of Chemistry,
University of Namur – UNamur, 5000 Namur, Belgique
E-mail: arnaud.osi@unamur.be

Due to their unique chemical, physical and photophysical properties, organoboron compounds and in particular triarylboranes derivatives are playing a central role in material science, supramolecular chemistry and catalysis.[1]

Triarylboranes are well-known boron Lewis acids which are widely used as catalyst for functional groups activation and, in combination with sterically demanding Lewis bases, for the activation of small molecules (H_2, CO_2, N_2O, …) in frustrated Lewis pair chemistry.[2] Some derivatives are also used as anion sensors or in materials for their optoelectronic properties.[3] Such boranes generally display a propeller like geometry with a central sp^2 hybridized trigonal planar boron atom.

Coercing the boron atom in a planar or pyramidal geometry leads to tremendous modification of their chemical (*e.g.* Lewis acidity) and physical (*e.g.* fluorescence) properties. We synthesized a collection of triarylboranes and investigated the effect of the structural constraints on this important class of Lewis acids using experimental methods combined with quantum chemical investigations.[4]

This talk will be mainly devoted to the synthesis of 9-boratriptycene, a triarylborane displaying a non-planar trivalent boron atom in the bridgehead position of a triptycene scaffold, as well as the investigations concerning the Lewis acidity and the electronic properties of this new class of boron Lewis acids.[5]

[1] "*Synthesis and Application of Organoboron Compounds*", Fernández, E.; and Whiting, A. Eds. Springer, New York, (2015).

[2] Stephan D. W.; and Erker, G. *Angew. Chem. Int. Ed.* ***54***, 6400 (2015).

[3] Hirai, M.; Naoki, T.; Sakai, M.; and Yamagushi, S. *Chem. Rev.* **14**, 8291 (2019).

[4] Doan, T.-H.; Chardon, A.; Osi, A.; Mahaut, D.; Tumanov, N.; Wouters, J.; Champagne, B.; and Berionni, G. *Chem. Eur. J.* Accepted Article

[5] Chardon, A.; Osi, A.; Mahaut, D.; Doan, T.-H.; Tumanov, N.; Wouters, J.; Fusaro, L.; Champagne, B.; and Berionni, G. *Angew. Chem. Int. Ed.* **59**, 12402 (2020).

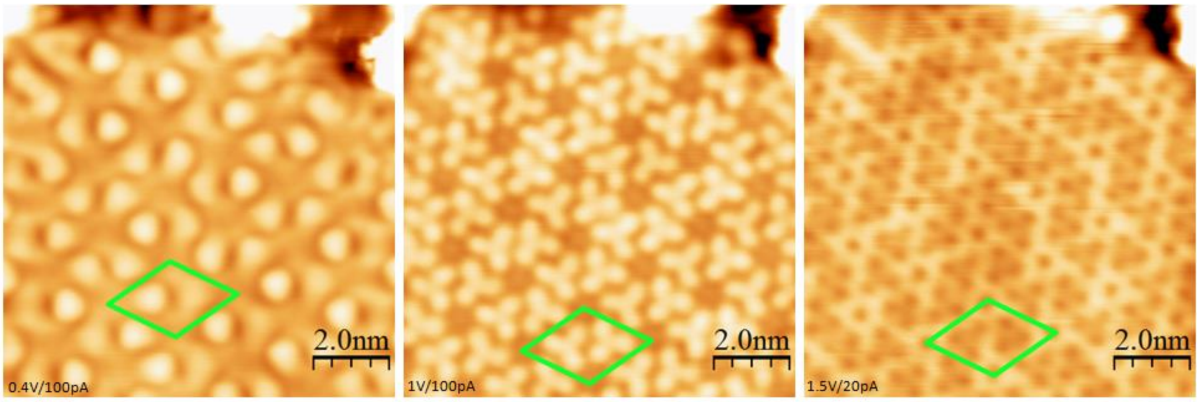
Structural and electronic properties of 1H-MoTe$_2$ films grown on graphene by molecular beam epitaxy

Trung T. Pham[1], Roshan Castelino[1], Peter Vancso[2], Luc Henrard[1], Jérome Lagoute[3] and Robert Sporken[1]

[1]*Namur Institute of Structured Matter (NISM), Department of Physics,*
University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium.
[2]*Nanostructures Department & 2D Materials ERC Research Group, Hungarian Academy of Sciences (MTA), Centre for Energy Research (EK), Institute of Technical Physics and Materials Science (MFA), Hungary.*
[3]*Matériaux & Phénomènes Quantiques, Université Paris Diderot-Paris 7, France.*

E-mail: trung.phamthanh@unamur.be

The direct growth of large area and high crystalline 2H-MoTe$_2$ films on graphene terminated 6H-SiC(0001) substrates by using molecular beam epitaxy with appropriate conditions was demonstrated [1]. In this research, we found that single-layer 2H-MoTe$_2$ on graphene induces the formation of different Moiré patterns and reveals very interesting surface structure of MoTe$_2$ films under various sample bias (see figure). In order to explain the structural and electronic properties of 1H-MoTe$_2$ films, in this work we present STM/STS data in combination with DFT calculation and simulation of STM images to understand the phenomena of such pattern formations in the films.



STM images of single-layer 2H-MoTe$_2$ on graphene under different sample bias (green rhombus indicates Moiré pattern $2\sqrt{7}R34.2°$).

[1] Pham, T.T.; Castelino, R.; Felten, A.; and Sporken, R., *Applied Surface Science* **523**, 146428 (2020).

Photodegradation of Rhodamine B dye by Al-doped ZnO nanoparticles

Alessandra Piras [1,2], Luca Fusaro [1], Peter Adriaensens [2], An Hardy [2], Carmela Aprile [1], Marlies Van Bael [2]

1. *Group of Applied Materials Chemistry (CMA), Chemistry department, University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*
2. *Group of Design and Synthesis of Inorganic materials (DESINe), Chemistry department, University of Hasselt, Campus Diepenbeek, Agoralaan building D, 3590 Diepenbeek, Belgium*

E-mail: alessandra.piras@unamur.be

ZnO is one of the most widely used semiconducting materials for the photodegradation of organic pollutants in water.[1] Due to its band-gap of 3.37 eV at RT, it mainly absorbs in the UV.[2] Since the UV light only accounts for the 4% of the total solar energy available on our planet, the inability to use the visible light limits the efficiency of ZnO as a photocatalyst for solar-based applications. To improve the visible-light response, the band-gap has to be fine-tuned. One effective way to narrow the band-gap is doping ZnO with post-transition metals such as aluminum. This dopant stimulates the formation of native defects in the ZnO lattice. Such defects generate mid-bandgap energy levels and thus should improve the sensitivity of the photocatalyst to the visible-light.[3,4]

Herein, Al-doped ZnO nanoparticles with different Al content were synthesized *via* a solvothermal route, and employed as photocatalysts for the degradation of Rhodamine B dye under UV and visible-light. A quantitative determination of the dopant incorporated into the final solid was estimated by inductively coupled plasma-optical emission spectrometry (ICP-OES). The morphology and the size distribution of the nanoparticles was evaluated by transmission electron microscopy (TEM). To investigate and determine any possible effects of the dopant on the zinc oxide structure, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and solid-state ^{27}Al nuclear magnetic resonance (NMR) have been used. The last technique provides information on the local environment of the Al ions inserted into the zinc oxide structure, and it is widely used to study the position of Al in the crystalline lattice.

The preliminary photocatalytic tests selecting RhB as target compound displayed that both undoped and Al-doped ZnO materials are active under UV-C, UV-A and visible-light irradiation, demonstrating their ability to remove the organic dye in water solution.

Considering the abovementioned, the final goal of this project aims to accurately assign the positions occupied by the Al into the ZnO crystal lattice. Furthermore, we will study in detail the connection between the photocatalytic activity of Al-doped ZnO under both UV and visible light in function of the positions occupied by the Al into the zinc oxide lattice.

1 Y. Liao, C. Xie, Y. Liu, H. Chen, H. Li and J. Wu, *Ceram. Int.*, 2012, 38, 4437–4444.

2 J. Wu and D. Xue, *Sci. Adv. Mater.*, 2011, **3**, 127–149.

3 F. Ajala, A. Hamrouni, A. Houas, H. Lachheb, B. Megna, L. Palmisano and F. Parrino, *Appl. Surf. Sci.*, 2018, **445**, 376–382.

4 R. Buonsanti, A. Llordes, S. Aloni, B. A. Helms and D. J. Milliron, *Nano Lett.*, 2011, **11**, 4706–4710.

Inverting the Singlet-Triplet Excitation Energy Gap in Triangle-Shaped Molecular Emitters

Gaetano Ricci

Unité de Chimie Physique Théorique et Structurale & Laboratoire de Physique du Solid,
Namur Institute of Structured Matter, Université de Namur, B-5000 Namur, Belgium
Email : gaetano.ricci@unamur.be

The full harvesting of both singlet and triplet excitons can pave the way towards more efficient molecular light-emission mechanisms (i.e., TADF or Thermally Activated Delayed Fluorescence) beyond the spin statistics limit [1]. This TADF mechanism benefits from low (but typically positive) singlet-triplet energy gaps. Recent results have suggested a possible inversion of the singlet-triplet excited states in triangle-shaped molecules (or triangulenes), opening a new pathway to improve the efficiency of organic light-emitting materials [2][3].
In this work, we have selected a set of heteroatom-substituted triangulenes for which is predicted $\Delta E_{ST} < 0$, highlighting the relevant role of the doubly-excited configurations to the S_1 and T_1 wavefunctions in the singlet-triplet inversion. Unfortunately, TD-DFT methods are unable to deal with the physical effects driving this behaviour; e.g., the large contribution of double excitations for all the ground- and excited-states involved, which prompted us to the use of more sophisticated ab initio methods such as SA-CASSCF, SC-NEVPT2, SCS-ADC(2), and SCS-CC2.

[1] Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. *Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes.* Applied Physics Letters **2011**, *98*, 42.
[2] Ehrmaier, J.; Rabe, E. J.; Pristash, S. R.; Corp, K. L.; Schlenker, C.W.; Sobolewski, A. L.; Domcke, W. *Singlet–Triplet Inversion in Heptazine and in Polymeric Carbon Nitrides.* The Journal of Physical Chemistry A **2019**, *123*, 8099–8108.
[3] de Silva P. *Inverted Singlet−Triplet Gaps and Their Relevance to Thermally Activated Delayed Fluorescence.* J. Phys. Chem. Lett. **2019**, *10*, 5674−5679

Synthesis of functionalized copillar[5]arenes and rotaxane as heteromultivalent scaffolds

Wenzhang Chen, Tharwhat Mohy El Dine, Stéphane Vincent

Laboratory of Bioorganic Chemistry,

Unamur, 61 rue de Bruxelles, 5000, Belgium

E-mail: chenwenzhang@unamur.be

Carbohydrate-protein interactions which organized in a cluster manner are ubiquitous in nature to achieved strong interaction and the "cluster" effect makes up a crucial step in many biological processes, such as cell adhesion, inflammation, and infection.[1] Carbohydrates present at the surface of cells binding to protein receptors that also called lectins or adhesins (excluding enzymes and immunoglobulins) frequently mediate the first step of the infection process for many pathogens including viruses, fungi, bacteria, and bacterial toxins.[2,3] Therefore, inhibition of these interactions by competition with glycoclusters, graft glycoside ligands on core scaffold, represents a promising therapeutic avenue.

Focusing on this strategy, our lab has synthesized several series "glycoclusters" targeting bacterial proteins. Some of these "glycoclusters" exhibited a potent inhibition of the adhesion of pathogenic bacteria.[4,5] Recently, our lab also demonstrated that pillar[5]arenes can be used as a core scaffold to build heteroglycoclusters designed to achieve a better selectively .[6]

Indeed, different core scaffolds endow glycoclusters with specific topology which highly affect the competition binding affinity and efficiencies.[7] Thereby, the novel core scaffolds allowing efficient attachment of several distinctive ligands are meaningful to develop hetero glycoclusters which could improve binding selectively, affinity and illustrate the mechanistic. In this study, two novel copillar[4+1]arenes were synthesized and served as central heteromultivalent scaffolds via orthogonal couplings with a series of biologically relevant molecules such as carbohydrates, α-amino acids, biotin and phenylboronic acid. Moreover, further modifications by introducing maleimides or cyclooctyne groups provided molecular probes adapted to copper-free click chemistry. Then, we generated an octa-azidated fluorescent rotaxane bearing two distinct ligands in a fully controlled manner.

[1] Wenzel, M.; Prochnow, P.; Mowbray, C.; Vuong, C.; Hoxtermann, S.; Stepanek, J. J.; Albada, H. B.; Hall, J.; Metzler-Nolte, N.; Bandow, J. E. *Front. Cell Dev. Biol.* **4**, 86 (2016).
[2] Bernardi, A.; Jimenez-Barbero, J.; Casnati, A.; De Castro, C.; Darbre, T.; Fieschi, F.; Finne, J.; Funken, H.; Jaeger, K. E.; Lahmann, M.; Lindhorst, T. K.; Marradi, M.; Messner, P.; Molinaro, A.; Murphy, P. V.; Nativi, C.; Oscarson, S.; Penades, S.; Peri, F.; Pieters, R. J.; Renaudet, O.; Reymond, J. L.; Richichi, B.; Rojo, J.; Sansone, F.; Schaffer, C.; Turnbull, W. B.; Velasco-Torrijos, T.; Vidal, S.; Vincent, S.; Wennekes, T.; Zuilhof, H.; Imberty, A. *Chem. Soc. Rev.* **42**, 4709-27 (2013).
[3] Imberty, A.; Varrot, A. *Curr. Opin. Struct. Biol.* **18**, 567-76 (2008).
[4] Durka, M.; Buffet, K.; Iehl, J.; Holler, M.; Nierengarten, J. F.; Vincent, S. P. *Chem. Eur. J.* **18**, 641-51 (2012).
[5] Munoz, A.; Sigwalt, D.; Illescas, B. M.; Luczkowiak, J.; Rodriguez-Perez, L.; Nierengarten, I.; Holler, M.; Remy, J. S.; Buffet, K.; Vincent, S. P.; Rojo, J.; Delgado, R.; Nierengarten, J. F.; Martin, N. *Nat. Chem.* **8**, 50-7 (2016).
[6] Vincent, S. P.; Buffet, K.; Nierengarten, I.; Imberty, A.; Nierengarten, J. F. *Chem. Eur. J.* **22**, 88-92 (2016).
[7] Sansone, F.; Casnati, A. *Chem. Soc. Rev.* **42**, 4623-39 (2013).

Supported organic semiconductors for visible-light-promoted efficient C-H arylation of different heteroarenes

Yeromina Alexandra [1], Davide Bonifazi [2], Carmela Aprile [1]

1) *Group of Applied Materials Chemistry (CMA), Department of Chemistry, University of Namur – Rue de Bruxelles, 61, 5000 Namur, Belgium*
2) *Bonifazi Research group, Institute of Organic Chemistry, Faculty of Chemistry, University of Vienna – Universitätsring 1, 1010 Vienna, Austria*

E-mail: oleksandra.yeromina@unamur.be

Metal-free visible-light-harvesting photocatalysis have recently emerged as a new and highly efficient sustainable tool in catalysis. Several transformations have been already achieved using this tool under homogeneous conditions, such as dehalogenation of different haloarenes, Aza-Henry or C-H arylation reactions. [1] These organic transformations are triggered by different polycyclic aromatic compounds, also called organic semiconductors (OSCs), able to absorb light in the visible region and to promote the formation of reactive radical species. Benzenediazonium salts are effectively employed as a source of benzene radicals, that once formed can couple with different heteroarenes. [2]

In this work some OSCs, such as *peri*-xanthenoxanthene mono- and diimide (PXXMI and PXXDI respectively) were synthetized and covalently anchored on mesoporous silica nanoparticles in order to generate heterogeneous photocatalysts active also in water-based media (Figure 1). The obtained solids were characterized by various techniques, including solid-state ^{13}C and ^{29}Si NMR, UV/Vis spectroscopy and N_2 physisorption. Their ability to trigger photocatalytic C-H arylation of different heteroarenes was compared to OSCs in homogeneous conditions, indicating their outstanding activity. The results indicate that the optophysical properties of the OSCs were preserved after heterogenization. Moreover, the solids were used in multiple cycles without decrease in their catalytic performances.

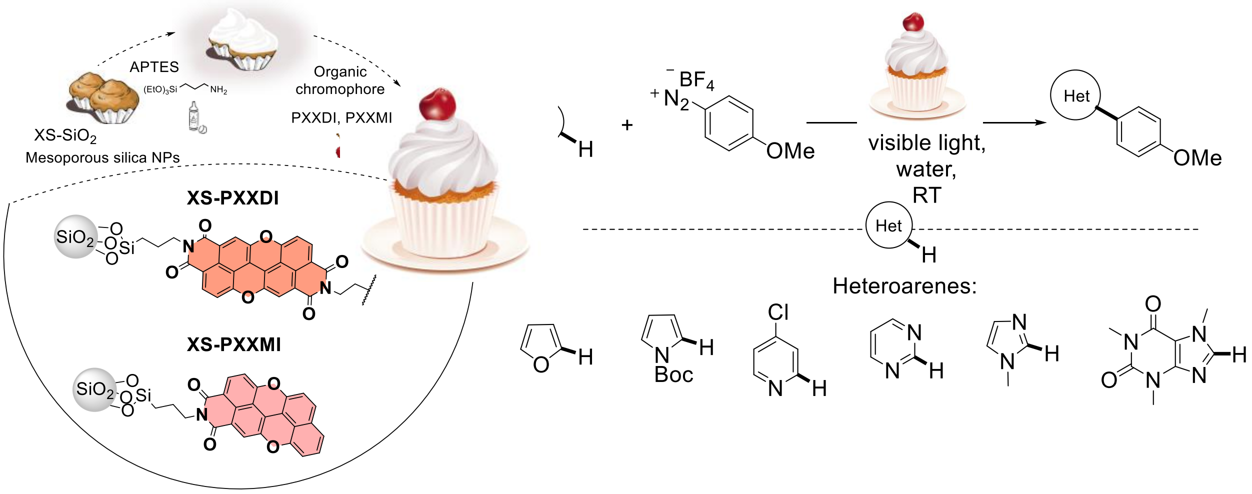


Figure 1. Synthesis of supported OSCs and their application for C-H arylation reaction.

[1] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566–1577.

[2] D. Xue, Z. H. Jia, C. J. Zhao, Y. Y. Zhang, C. Wang, J. Xiao, *Chem. - A Eur. J.* **2014**, *20*, 2960–65.