

Annual NISM meeting 2023

Terra Nova, Citadel of Namur
December 18th 2023

Welcome, Prof. Vincent Liégeois: 9:00–9:10

Session 1, chair: Carmela Aprile, Anthony Morena

David Cannella <i>(invited Talk)</i>	“The push-forward role of Biofuels in the modern Biorefinery and in Bio Sustainable society”	9:10–9:50
Julien Bouchat	“Coherent scattering in quasi-ordered structures gives rise to the blue colour of the bluespotted ribbontail ray”	9:50–10:05
Chloé Célis	“Design of bifunctional silica-based nanotubes for the catalytic conversion of carbon dioxide into cyclic carbonates”	10:05–10:20

Flash poster session (3 minutes each): 10:20–10:35

Dorothee Brandt	“Coarse-graining PBTTT, a semi-conducting polymer”
Maxime Mathieu	“Towards Shape-Tunable Hierarchical TiO ₂ Single Crystals as Catalyst for CO ₂ Valorization”
Komlanvi Sèvi Kaka	“Third-order nonlinear optical properties of organic p-conjugated molecules: quantum chemistry studies and comparison with experiment”
Vittorio Marsala	“Towards the understanding of the formation mechanism of hollow silica nanotubes and nanospheres: an NMR approach”
Nicolas Niessen	“Development and Lewis Acidity of Pyramidal Triarylborane and Borenium Ions”

Coffee break and poster session: 10:35–11:00

Session 2, chair: Emile Haye

Mathias Fraiponts	“Rational Design and Synthesis of Pyrrolopyrrole Aza-BODIPY Photosensitizers for Image-Guided Photodynamic Therapy”	11:00–11:15
Alireza Bagherpour	“Vein pattern vs. columnar fracture shape in Cu-Zr thin film metallic glasses: Driving force and mechanism”	11:15–11:30
Xikun Zhang	“Dual ions co-intercalation induced spontaneous and reversible phase replacement chemistry enables superior Zn ²⁺ storage”	11:30–11:45
Danillo Pires Valverde	“Computational Insights into the Photophysics of Inverted Singlet-Triplet Gap Materials”	11:45–12:00

Intervention de Murielle Guillaume,
responsable cellule emploi du SRH de l'UNamur: 12H00–12H30

Lunch and poster session: 12:30–13:35

Session 3, chair: Yoann Olivier, Gaetano Ricci

Claire Tonnelé <i>(invited Talk)</i>	“Chasing neutrino’s nature: Ba ²⁺ luminescent sensing from a computational perspective”	13:35–14:15
Nicolas Roy	“Utilizing highly data-efficient computational intelligence for the engineering of photonic devices: a case study on vortex phase mask coronagraphs”	14:15–15:30
Kajetan Bijouard	“B-YOND: Reprogramming the reactivity of main-group elements”	15:30–14:45
Loris Chavée	“Growth mechanisms and properties of magnetron sputtered TiO ₂ thin films on complex 3D foam substrates”	14:45–15:00

Coffee break and poster session: 15:00–15:25

Session 4, chair: Francesca Cecchet

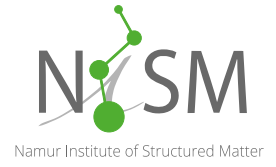
Adrien Debacq	“Crystal Clear Dirac Cone Prediction in Photonic Band Structures”	15:25–15:40
Mohamed Achehboune	“Atomistic insights into nucleation and growth of hexagonal Boron Nitride on Germanium”	15:40–15:55

Conclusions, Prof. Francesca Cecchet: 15:55–16:00

Drink: 16:00–17:00

Poster sessions

Mohamed Chellegui	“Exploring Reaction Mechanism of Diels-Alder Cycloadditions between Furan-Based Dienes and Ethylene Derivatives. A Study from the Perspective of Bond Evolution Theory”
Jun Chen	“Inverse opal material photocatalyst for enhanced light absorption facilitates photocatalytic conversion of renewable and low value biomass into value-added chemicals”
Lou D’haese	“Surrounding effects on Raman optical activity signatures”
Alban de Gary	“Maximizing light outcoupling in OLEDs: insights from molecular simulations”
Oliver Garot, Anthony Morena	“Understanding the acidity properties of different silica-based materials via ³¹ P ssNMR using TMP as probe molecule”
Laurelenn Hennaux	“Structural and functional characterization of a copper efflux membrane protein: PcoB from <i>Caulobacter crescentus</i> ”
Valentin Job	“Investigation of the Antimicrobial Properties of Thin Films Produced by Low Pressure Magnetron”
Jing Li	“Hierarchical Heterostructured Cathode for a Visible-Light-Involved in Lithium–Oxygen Battery”
Zhonghao Miao	“Tailoring short-chain sulfur molecules to drive redox dynamics for sulfur-based aqueous battery”
Thanh Trung Pham	“Investigation of 1H-MoTe2 doped with nitrogen”
Gaetano Ricci	“Exploring the electronic structure of extended triangulenes: opening new doors for a fast Reverse Intersystem Crossing”
Martina Saitta	“Conversion of glycerol into solketal catalyzed by hybrid porous zirconium(IV) phosphonate networks”
Tanguy Scaillet	“Towards the Development of Covalent Inhibitors for <i>Brucella</i> <i>Militensis</i> SerB through Crystallography and Kinetics”
Laura Valentino, Chloé Célis	“Phosphonium Salt/Al-Porphyrin Copolymer as Bifunctional Heterogeneous Catalyst for CO ₂ Conversion to Cyclic Carbonates”
Guanying Wang	“Synthesis of Hierarchical Single-Crystal ZSM-5 and SAPO-34 Zeolite”
Yuanguo Wu	“Sharing Electronic and Ion Transfer Channels by In-Situ Integration of Gel Polymer Electrolyte for Solid-State Lithium-Oxygen Battery”
Hao Xu	“Impact of Mo/W distribution on the properties of Keggin catalysts”
Liuxi Yang	“Non-covalently synthesis of porous organic salts”
Runtian Zheng	“Integrated insights into NH ₄ ⁺ storage mechanism and electrochemical kinetics of ultrastable Prussian blue analogues for Ammonium-Ion Battery”



Plenary Abstracts

Ass. Prof. David Cannella,
ULB – Ecole Bioingénierie de Bruxelles, PhotoBiocatalysis Unit

Seminar : NISM 2023, Namur

Title

"The push-forward role of Biofuels in the modern Biorefinery and BioSustainable society"

Abstract

Since the first oil crisis in the '70s several countries started to develop research programs for development of alternative fuels all based on renewable biomass. The first generation encompassed biotransformation of potatoes, sugar cane or corn to obtain BioEthanol via fermentation of starch or sucrose. Also vegetable oils extracted from food-stocks like palm fruits or various seeds were transformed in BioDiesel. Despite the success in producing biofuels at good yield and the unraveled environmental benefits towards petrol-fuels, evident ethical limits arose due to the withdrawing of potential food resources towards an ever growing amount of starving human beings. Therefore alternative processes were demanded by the society: as such a second generation of biofuels technology was set successfully around the first decade of 2000s encompassing this time only the not-edible part of the plants or lignocellulosic waste of any sort from the industrial agro/forest sectors. The key factor unlocking such potential had been the development of new biotechnologies based on enzymatic biocatalysis such as cellulase, lipases, laccases, ligninase and more, able at depolymerizing the hardest renewable biopolymer such as lignocellulose, lipids and chitin in precursors of BioEthanol and BioDiesel. Yield efficient industrial demo-plant had been then inaugurated worldwide particularly in Europe, and the paradigm shift from 1 single product-biotransformation to a variety of bioproducts was immediately obtained by the collateral production of essential chemicals, biomaterials or bioenergy as by-product of the originally intended main biofuel product. Indeed the development of bioprocesses for the production of biofuels gave birth to what is today known as Biorefinery, a sector able at providing raw materials for uncountable different bioproducts spanning from biomaterials, nanotechnologies, food ingredients, prebiotics, biopesticides, biofertilizers, food packaging, bioplastics, biochemical additives, cosmetics, furniture and more. Eventually the talk will also touch upon new frontiers of Biorefinery research like the Photo-BioCatalysis that aims at carrying the above mentioned enzymatic reactions using the light's energy, as such a BioPower-to-X technology using new classes of redox and photo-excitabile enzymes.

Chasing neutrino's nature: Ba²⁺ luminescent sensing from a computational chemistry perspective

Many open questions remain in the field of particle physics, and, among them, the matter/antimatter imbalance is one of the most compelling. According to the Big Bang theory, equal amount of matter and antimatter were created during the formation of the universe. As they annihilate on contact, we should have been left with nothing but pure energy. Yet, something must have tipped off the balance as we live in a world dominated by matter. The key to that mystery could come down to a particle that must have behaved inconsistently with the current physics model to break the matter/antimatter symmetry, the neutrino.

Physicists are looking for answers in a rare particle process called the neutrinoless double β -decay. In a regular double β -decay, two neutrons of a nucleus decay into two protons, emitting two electrons and two antineutrinos. However, if the neutrino were its own antiparticle, only two electrons would be emitted, thus violating the expected particle conservation. To distinguish this very elusive process from background radioactivity, high resolution setups with background discrimination are necessary. One possible way to reach background-free experiment lies in the in-situ detection of the daughter atom of the decay together with the signature of the two emitted electrons. That is where particle physics meets fluorescent chemosensing.

A molecular chemical sensor consists in a recognition unit, responsible for the selective binding of a given species, covalently linked, by a spacer or not, to a chromophore. The capture of the analyte translates into a modified optical signal of the chromophore, the detection generally relying on an on/off emission behaviour or a fluorescence spectral shift. In the first case, the on/off ratio in intensity must be large to obtain reliable measurement. In the second one, the spectral shift must be significant enough to ensure clear signal of the complexation. These drawbacks can cause serious limitations when considering a dense sensor layer where a molecule capturing the analyte is surrounded by many unchelated sensors. An alternative to circumvent these issues is to impart the chemosensor with temporal resolution, that is, the free and chelated states would emit in different regimes, namely fluorescence and phosphorescence. In this talk, I will present the computational study of Ba²⁺ chemosensors designed in the context of the Neutrino Experiment with Xenon TPC (NEXT) experiment, within the BOLD Synergy Project (<https://next.ific.uv.es/next/>).

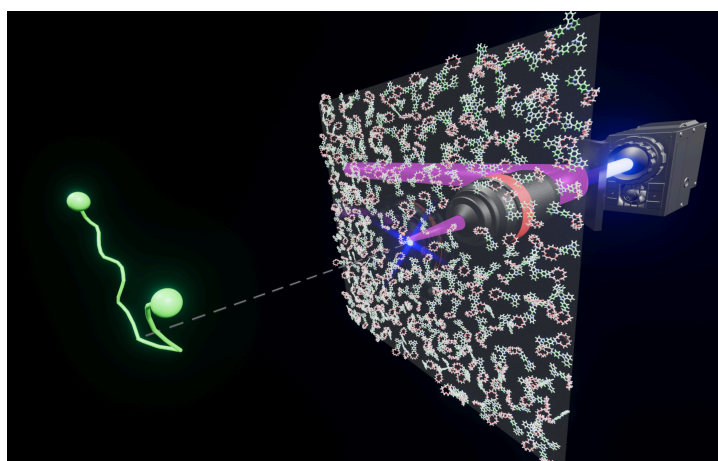
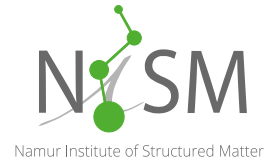


Image courtesy of Dr. Pablo Herrero Gómez



Oral Abstracts

Coherent scattering in quasi-ordered structures gives rise to the blue colour of the bluespotted ribbontail ray

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Blue is often described as the rarest colour in natural organisms [1]. Elucidating the underlying mechanism(s) giving rise to such a hue is always very impactful for the understanding of the natural world in which human beings live. Moreover, fishes are one of the least studied organisms in natural photonics [2].

In this talk, I will explain how the colour of the blue rounded spots occurring in the skin of the bluespotted ribbontail ray *Taeniura lymma* was unveiled by a combination of experimental and numerical techniques. For this purpose, histological observations were carried out with optical, fluorescence and transmission electron microscopies and the optical characterizations were performed by spectrometry and microspectrofluorimetry. In order to highlight the response of these structures with visible light, numerical simulations were based on two-dimensional fast Fourier transforms of electron micrographs of the observed structures and Benedek's theory relating Fourier transform of spatial variation in refractive index to the intensity of coherent scattering [3].

I will thus outline that our results demonstrated that the blue colour of this ray arises from coherent scattering in quasi-ordered photonic structures occurring in the skin of this animal. This type of bidimensional structures made of collagen fibres is mostly unknown in marine species. In addition, structural blue colours had never been reported in elasmobranchs.

[1] Mouchet, S. R. and O. Deparis, Natural Photonics & Bioinspiration, Boston: Artech House, 2021.

[2] Shuichi Kinoshita. Structural colors in the realm of nature. World Scientific, 2008.

[3] Benedek, G. B., "Theory of Transparency of the Eye," Applied Optics, Vol. 10, No. 3, 459-473, 1971



Figure 1. The blue spots occurring in the integuments of *T. lymma* arise from quasi-ordered photonic structures. Photograph by Taken reproduced from <https://pixabay.com/photos/ray-stingray-fish-sea-ocean-539788/>

Design of bifunctional silica-based nanotubes for the catalytic conversion of carbon dioxide into cyclic carbonates

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In the context of green chemistry, the conversion of carbon dioxide into added value products, such as cyclic carbonates, is particularly interesting, as it allows valorizing a waste and employing a renewable source of carbon. To achieve the transformation of this very stable molecule (CO₂), high energy reactants, such as epoxides, combined with a catalyst should be employed. Imidazolium salts have proven to be particularly efficient as homogeneous catalysts for this reaction.^[1] However, for sustainability reasons, it is interesting to graft this active moiety on a solid support, in order to have a heterogeneous system that can be easily recovered from the reaction medium and reused. In this context, silica-based nanotubes with their elevated specific surface area, their open-ends and high accessibility of the active sites are promising candidates as solid support.^[2,3] Moreover, one of the most appealing properties of such silica-based material is the possibility to create Lewis acid sites in the framework, via the isomorphic substitution of silicon atoms with suitable elements. These metal centers can activate epoxides and therefore act as co-catalyst in the target reaction.

In this work, the use of hafnium^[2] and tin^[4] cations is investigated, using two different Si/M ratios of 74 and 37. Hafnium-doped and tin-doped silica nanotubes functionalized with imidazolium moieties were successfully synthesized. The different characterization techniques confirmed the interesting features of the solids, such as the tubular morphology, the meso-porosity, the high specific surface area, the efficient insertion of the metal cations in the silica structure, the acidity of the solids, as well as the correct grafting of imidazolium species. The synthesized catalysts were then tested for the valorization of CO₂ with styrene oxide, all of them were active and highly selective. The two materials with the better catalytic performances (Si/M = 74) were then selected to continue the investigations and have proven to be stable and recyclable. The versatility of the Hf-based material was finally confirmed using different epoxides. Finally, by tuning the reaction conditions or changing the counterion of the imidazolium salt, a further improvement of the catalytic performances was obtained.

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Rational Design and Synthesis of Pyrrolopyrrole Aza-BODIPY Photosensitizers for Image-Guided Photodynamic Therapy

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With its strong absorption and emission in the near-infrared range, the recently developed pyrrolopyrrole aza-BODIPY (PPAB) has brought the all-round great characteristics of the well-known BODIPY dye class to a new part of the spectrum, proving itself useful in applications ranging from organic photovoltaics to bio-imaging.^[1] Yet, the properties of PPAB dyes are most effectively leveraged by the field of photodynamic therapy (PDT) as the majority of its derivatives are active within the so-called phototherapeutic window (600–800 nm). PDT is an up-and-coming form of phototherapy capable of eliciting targeted cell death via a combination of molecular oxygen and a selectively irradiated photosensitizer (PS). As of today, the overall potential of PDT is far from realized as the efficacy of commercial PSs is held back by their rather weak absorption at unfavorable wavelengths, lack of phototoxic power, non-negligible dark cytotoxicity, and prolonged skin photosensitivity.

This contribution explores the adaptation of PPAB fluorophores to photosensitizers via the spin-orbit coupled charge-transfer intersystem crossing (SOCT-ISC) mechanism, which achieves efficient generation of long-lived triplet states without the use of cytotoxic heavy atoms.^[2] Several donor-acceptor type structures were conceived through density functional theory mediated rational design, using existing and newly fashioned charge-transfer analysis methods. Careful tuning of the charge-transfer properties enabled the partial preservation of fluorescence, rendering a single compound fit for both PDT and image-mediated diagnostic applications. Our compounds yielded various ratios of phototoxicity versus fluorescence, some with high combined quantum yields. Overall, the properties depend strongly on the donor strength and positioning, providing valuable insights into the excited-state behavior of donor-acceptor type PPABs.

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Vein pattern vs. columnar fracture shape in Cu-Zr thin film metallic glasses: Driving force and mechanism

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Shear bands, localized regions of intense shearing strain, are common in various materials but are particularly prominent in metallic glasses due to their work-softening behavior below the glass transition temperature (T_g) [1]. The occurrence of shear bands limits the structural potential of metallic glasses as they lead to plastic instability and catastrophic failure under tension [2]. During shear banding, the stored elastic energy converts into kinetic energy within the bands, resulting in a temperature rise. The fracture of metallic glasses (MGs) exhibits distinct features such as spark formation, liquid droplets, and river-like patterns, indicating a significant temperature increase (thousands of degrees) during fracture [3].

Numerous studies have been published in the past showing the presence of vein-like or columnar fracture shapes in thin film metallic glasses (TFMGs), while the reason behind the different features remains poorly understood. This study uncovers the reason behind this phenomenon in Cu-Zr TFMGs' by considering experimental evidence and analysis. Oxidation during deposition is the reason for the presence of the columnar feature after the cleavage, as shear banding cannot raise the temperature enough for the regional melting process to end up in the vein pattern. In several studies, unnoticed or unreported oxygen is proposed to be the reason for reporting metallic glasses' columnar cross-sections.

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Dual ions co-intercalation induced spontaneous and reversible phase replacement chemistry enables superior Zn²⁺ storage

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Prussian blue analogues are highly promising electrode materials, however, they suffer from severe structural damage caused by the dissolution of high-spin outer metal ions, that results in poor cycle life. Material modification and electrolyte regulation have been the common approaches to address this issue, albeit with limited success. We report here a novel and efficient co-intercalation process via electrolyte regulation that involves a spontaneous and reversible phase conversion induced by the replacement of low-spin inner ion (Fe³⁺) by Co²⁺ and Zn²⁺ ions co-intercalating in KCo[Fe(CN)₆]. This phase replacement approach, which is different from the conventional phase conversion approach featured by the replacement of high-spin outer ions, was able to effectively relieve structural deformation caused by Jahn-Teller distortion and metal-ion dissolution, thereby resulting in an exceptional improvement of cycle life with a capacity retention of 97.7% over 4400 cycles at 40 C.

Computational Insights into the Photophysics of Inverted Singlet-Triplet Gap Materials

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One of the major challenges in Organic Light Emitting Diodes (OLED) is the improvement of the internal quantum efficiency (IQE) since the spin statistics recombination limits it to only 25% for closed-shell fluorescent emitters [1]. Several experimental and theoretical designs of new emitters have been proposed over the years in order to recover the lost triplet population. Recently, the fourth generation of OLED emitters, as known as inverted singlet-triplet gap materials (INVEST), have received a great attention because the lowest singlet excited state (S_1) is energetically lower than the lowest triplet excited state (T_1) in these compounds. Accordingly, this implies the breakdown of Hund's rule and makes the reverse intersystem crossing (rISC) from triplet to singlet manifolds an exothermic path that can potentially lead to a triplet harvesting enhancement. With these premises, the present work aims to understand the photochemical relaxation mechanisms from a theoretical point of view of three workhorse triangle-based compounds (cyclazine, pentazine, and heptazine) that exhibit the attractive features of INVEST materials. To this end, the most relevant minima, conical intersection, and intersystem crossing structures in different potentials energy surfaces (PES) were optimized using the XMS-CASPT2 and SCS-ADC(2) methods. Our results suggest that only S_1 and T_1 states are part of the ISC and rISC mechanisms given that other excited states are located in a much higher energy. We were also able to understand why cyclazine exhibits an anti-Kaska emission when photoexcited to the S_2 state [2]. By including non-Condon effects within the Herzberg-Teller (HT) approximation, we identified which normal modes contribute more to the increase of the spin-orbit coupling (SOC). Additionally, within the crude approximation [3], we rationalized which higher-lying singlets (triplets) are vibronically coupled with the lower-lying singlet (triplet), which helps us to better understand the HT contribution to the SOC observed for the three compounds.

[1] Uoyama, H. *et al.* *Nature* **492**, 234–238 (2012)

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Utilizing highly data-efficient computational intelligence for the engineering of photonic devices: a case study on vortex phase mask coronagraphs

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This study leverages various computational intelligence (CI) techniques to devise optimal designs of complex photonic devices. The interplay between the geometric parameters of such devices and their performance leads to a vast design space where optimization requires a lot of simulations to achieve a breakthrough in performance.

A practical limitation arises due to the considerable computation time typically required for simulations, which is commonly addressed by employing surrogate models such as partial least squares Kriging, radial basis functions, or neural networks. These surrogate models once appropriately trained provide swift evaluations of the device performance to the optimization algorithm.

However, our study demonstrates that these methods are inadequate in modeling the performance of complex photonic devices, such as a vortex phase mask (VPM) [1,2]. VPMs play a crucial role in enabling astronomers to observe faint light sources near bright objects, such as exoplanets near stars. The core of the VPM comprises a diamond substrate etched with a specific pattern to be optimized, forming a phase plate positioned at the focal plane of a telescope.

A data-efficient surrogate optimization setup using a deep neural network (U-Net) as surrogate model [3] and particle swarm optimization is proposed. In this setup, the model and optimizer gradually explore the search space by performing fully-fledged simulations only on key devices. The U-Net is shown to be both extremely accurate and efficient, achieving correlation coefficients greater than 98%. Optimal VPM designs are finally devised using this framework, achieving better results with fewer simulations than optimizations based on systematic evaluations of parameter combinations on a grid [2].

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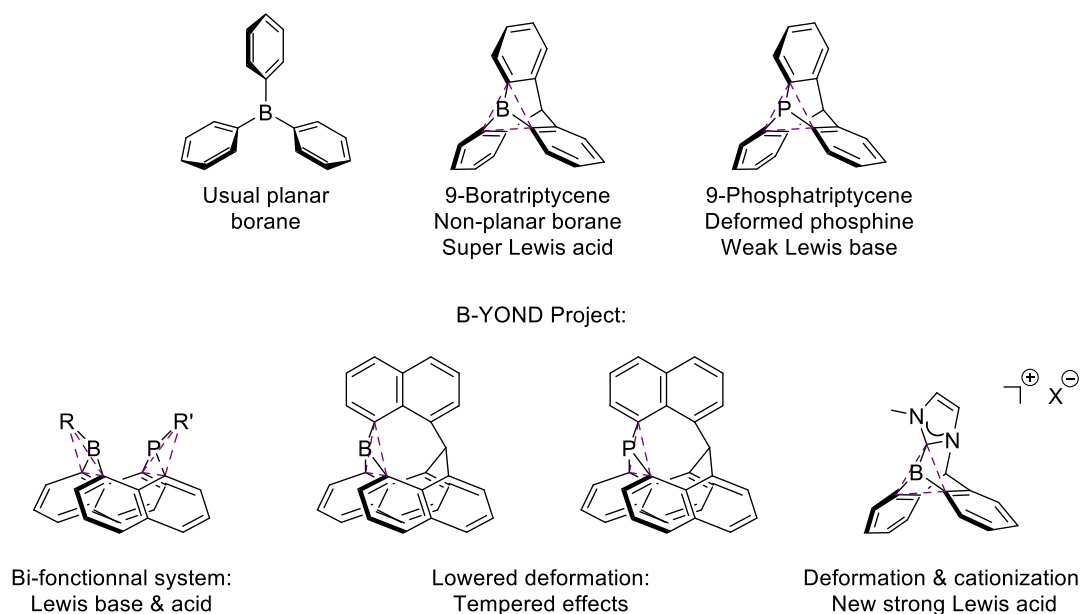
This study employs computational intelligence techniques to optimize complex photonic devices. Traditional surrogate models have limitations in accurately modeling complex devices like vortex phase masks (VPMs). VPMs are essential for observing faint light sources near bright objects, such as exoplanets near stars. To address this, a data-efficient surrogate optimization setup using a deep neural network (U-Net) and particle swarm optimization is proposed. The U-Net achieves high accuracy and efficiency. The resulting surrogate optimization setup outperforms both carefully devised grid-based searches and optimizers.

B-YOND: Reprogramming the reactivity of main-group elements

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Nature dictates the essence of the chemical bond: strength, valency, geometry. For decades, chemists have been fascinated by testing the limits of what Nature allows them to do. To this end, methanium cation (CH_5^+)^[1] or carboranes were, for example, synthesized.^[2] An important challenge lies in the control of the geometry of elements. For this purpose, triptycene scaffolds were used to force the pyramidalization of several heteroatoms. Pyramidalization of boron centres, as in 9-boratriptycene, leads to a dramatic increase of the Lewis acidity of the boron atom.^[3] The formed Lewis super-acid can, however, not exist in its free-form but can be present as a transient specie in several reactions.^{[3][4]} On the opposite, the pyramidalization of a phosphorus atom leads to an important decrease in its Lewis basicity.^[5] Drawn from these results, the B-YOND project aims at a better control of these geometrical deformations. The use of naphthalene units, instead of benzene, will lower the deformation of both Lewis acids and bases, allowing the access to new catalytic centres for which the modulation of the geometry should regulate the reactivity. Finally, we decided to perform the challenging synthesis of a geometrically deformed borenium cation, going against two of Nature laws: the neutral behaviour of trivalent boron and its, theoretically, trigonal planar geometry.



References

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Growth mechanisms and properties of magnetron sputtered TiO₂ thin films on complex 3D foam substrates

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The deposition of functional materials on foam substrates, particularly for photocatalytic applications [1], [2], is growing in importance. Coatings on foams are most of the time synthesised using chemical methods. PVD methods are rarely used to coat such substrates and when it is, the growth mechanisms are never mentioned. However, PVD deposition can bring significant interest on those complex 3D foam substrates, such as accurate control and tuning of film morphology, composition, and/or synthesis of metastable phases.

The scope of this work is to study the growth and properties of TiO₂ films deposited on Ni and C foams by the means of DC magnetron sputtering and HiPIMS, and to get insights on how the film grows on such complex 3D substrates, especially regarding the crystal structure of the coating inside the foam and how it relates to photocurrent generation.

The properties of the deposited films are investigated using XPS, SEM and XRD, while the photocatalytic performances of the TiO₂@Ni foam and TiO₂@C foam assemblies are studied by photoelectrochemical measurements. Thanks to high resolution XPS spectra, the chemical environment as well as the stoichiometry are studied. SEM cross sections of the TiO₂@C foam assemblies allow to observe the change in coating morphology with increasing depth inside the foam. XRD confirms the synthesis of crystalline TiO₂, whose structure is either anatase, or a mix of anatase and rutile depending on the deposition technique. The photoelectrochemical measurements, combined with the XRD results, highlight the superior photocurrent generation provided by the samples displaying a high number of {001} anatase crystal facets.

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Crystal Clear Dirac Cone Prediction in Photonic Band Structures

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A Dirac cone is characterized by a linear and isotropic dispersion in analogy with graphene [1]. The presence of a Dirac cone in the band structure of photonic crystals holds particular significance, especially in the context of near-zero refractive index media. Such materials exhibit special properties, including a uniform phase distribution and an infinite wavelength within the material [2]. If the photonic crystal is designed in such a way that the Dirac cone occurs at the Γ point of the Brillouin zone, an effective near-zero refractive index can be considered [3,4].

To predict the formation of Dirac cones, developing simple methods becomes crucial. It was found that an accidental degeneracy between modes belonging to certain irreducible representations of the crystal space group guarantees the formation of linear dispersion Dirac cones [5]. In this regard, an approach based on the link between crystal symmetry and group theory is proposed, using the tight-binding formalism to calculate band structures. Based on its symmetry alone, this method allows the identification of sufficient conditions for the presence of a Dirac cone, and hence a near-zero refractive index.

The validation of the theoretical predictions for a triangular lattice was carried out through comparisons with numerical simulations using the finite element method. We checked that the Dirac cone, for a laterally infinite structure, originates from the overlap between the doubly degenerate mode of the E_2 irreducible representation with a singly degenerate mode of the B_1 irreducible representation of the C_{6v} point group at the Γ point.

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Atomistic insights into nucleation and growth of hexagonal Boron Nitride on Germanium

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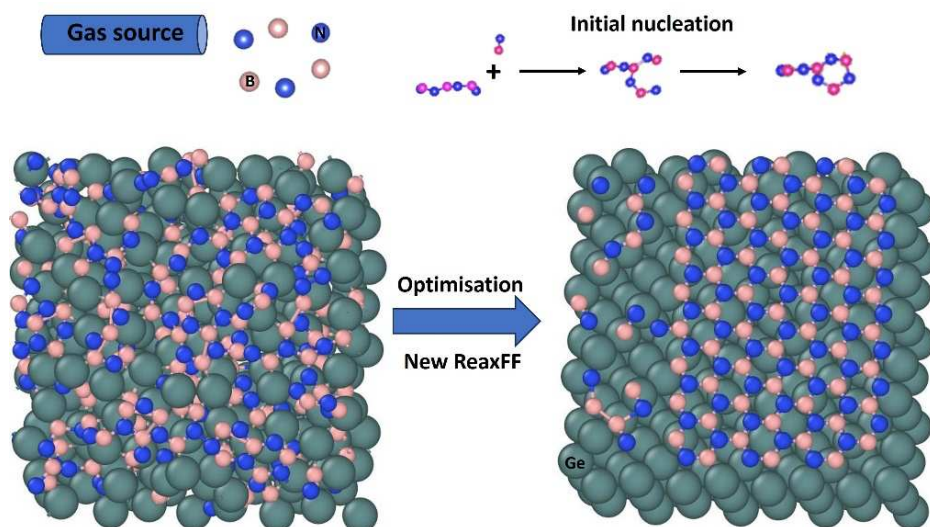
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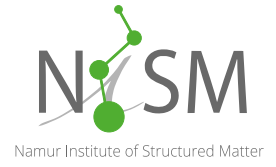
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The synthesis of large scale 2D materials is still an experimental challenge which slows down the implementation of the numerous technological application promises. A numerical investigation of growth process requires multiscale approaches. Indeed, the adsorption and diffusion of atomic species or small clusters can only be correctly described by purely quantum simulations, limited to a few hundreds of atoms where the complexity of the surface reaction implies in the growth requires to consider much larger systems.

A few layers of hexagonal boron nitride (hBN) form a 2D materials with interesting insulating properties which is an ideal template to growth perfectly crystalline and flat graphene (or other 2D materials). In this study, using a multiscale modelling approach that combines density functional theory (DFT) and molecular dynamics based on adapted reactive force field (ReaxFF) formulation, we explore the initial stage of the hBN growth on Ge(001) within an European FLAG-ERA project. The binding and the minimum energy path of atomic species and small clusters are investigated by DFT as well as the nucleation of larger hBN domain by molecular dynamics. We have observed the importance of subsurface diffusion of atomic B and N, leading to a disordered first layers of the Ge in agreement with experimental observation. Structures with a continuous hBN lattice are well established on the substrate surface. This study provides fundamental insights into crystal quality and the effect of temperature and substrate properties on hBN growth which could provide valuable guidance for manipulating the CVD synthesis of hBN on germanium substrates with enhanced precision and control.

Graphical Abstract





Poster + Flash Abstracts

Coarse-graining PBTTT, a semi-conducting polymer

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The use of semi-conducting polymers in the field of organic electronics has opened the door to flexible electronics.^[1] The flexibility of these materials is characterized by their mechanical properties which can be studied experimentally but also from a computational point of view.^[2, 3] In the latter, all-atomistic molecular dynamics are widely employed. However, using a coarse-grained (CG) model allows to reduce the computational time by using beads gathering together groups of two to four atoms.^[4] This enables to work on larger systems with system sizes closer to the experiments.

The Martini model is a widely spread force field used for CG simulations.^[5] Among the various applications of this force field, it has been employed for simulations of the poly(3-hexylthiophene) (P3HT), a state-of-the-art semi-conducting polymer.^[6] Inspired by the CG design of P3HT, we choose to coarse grain poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT). Coarse graining PBTTT is a strategic choice as its chemical structure is close to P3HT while exhibiting improved charge transport mobility, a key factor for electronic devices.^[7]

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Towards Shape-Tunable Hierarchical TiO₂ Single Crystals as Catalyst for CO₂ Valorization

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For years, reducing carbon dioxide emissions into the atmosphere has been a major priority. Among the possible abatement methods, the revalorization of CO₂ into value-added compounds such as methanol by catalytic processes remains one of the most promising solutions^[1]. In order to obtain better properties and more efficient catalysts, it is therefore necessary to improve and rethink the catalysts currently in use.

Since the discovery of its high efficiency in water splitting under ultraviolet light, titanium dioxide (TiO₂) has experienced a remarkable boom in the field of photocatalysis. Indeed, this material features semiconducting properties with a wide bandgap, and is highly abundant, available and stable^[2]. Among its various crystalline phases, anatase-TiO₂ single crystals (ASC) stand out for their highly reactive crystalline facets, which promote electronic transfer, interactions and enhance the kinetics of catalytic reactions^[3]. The efficiency of anatase crystals in catalyzing redox reactions is highly dependent on the exposure ratio of their *001* to their *101* facets^[4]. Compared to nanocrystals, ASC with long-range crystalline order can also prevent carriers trapping or recombination at grain boundaries, which could significantly enhance the performance of the device^[4]. As the efficiency of these crystals is mainly limited by their low specific surface area, the development of large single crystals with a hierarchical porous structure should greatly enhance the materials' performance in photocatalytic processes. The recently developed hierarchical zeolite single crystals with interconnected micro-meso-macropores, designed by Sun *et al.*, exhibit a very high specific surface area (up to 844m²/g)^[5]. This porous structure allows a better diffusion of gaseous species towards the active sites and a better catalytic conversion over the time^[5].

Therefore, the design of new catalysts based on hierarchical porous anatase single crystals seems a very attractive solution to improve the conversion of carbon dioxide into value-added products. For this reason, this work focuses on the impact of synthesis and crystallization conditions on the percentage of exposed facets and the shape of ASC, as well as the formation of hierarchical single crystals with interconnected porosity using a hard templating method.

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Third-order nonlinear optical properties of organic π -conjugated molecules: quantum chemistry studies and comparison with experiment

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Recent measurements of the second hyperpolarizability (γ) using Third Harmonic Scattering (THS) experiment have opened a new direction for calculating and interpreting γ .^{1,2} In the present work, quantum chemistry (QC) calculations, which are useful for rationalizing experimental data, are performed for evaluating γ of the prototype π -conjugated systems such as *p*-nitroaniline, *trans*-stilbene, and *cis*-stilbene using the CCSD(T) method as reference.

The γ quantities were calculated using the finite field (FF) method in the combination with the Romberg's quadrature allowing to improve the numerical derivatives. After selecting optimal parameters and reliable atomic basis set, electron correlation in wavefunction methods was shown to be far from negligible, while MP2 offers the best accuracy/cost ratio for computing the static γ . At DFT level, the crucial role played by the exact Hartree-Fock exchange, and the dynamic correlation was highlighted. Among the selected XCFs, the double-hybrid B2-PLYP functional provides accurate static γ values for *p*NA³ while range-separated hybrid functionals as CAM-B3LYP and ω B97X-D are reliable for the stilbene isomers. Then, the frequency dispersion effects were characterized using a polynomial in the effective frequency (in gas phase and in solution).

Finally, for stilbene various third order responses were estimated and compared to experiment. These comparisons evidenced that at large laser frequency (visible and beyond) the experiment-calculations comparisons are very difficult. Sometimes, there even appears inconsistency between experimental data. On the other hand, the agreement is good for near infrared (NIR) frequencies.

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Towards the understanding of the formation mechanism of hollow silica nanotubes and nanospheres: an NMR approach

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In the last 20 years, many low-dimensional porous silica-based nanomaterials have been synthesized via the sol-gel process and the micelles-templated syntheses of mesoporous solids. Among them, hollow nanospheres and nanotubes have withdrawn a great interest because of their elevated specific surface area and large pores diameter, which are favorable features for catalytic applications.^[1] Moreover, the isomorphic substitution of the Si with a metal cation allows obtaining an acid heterogeneous catalyst.^[2]

It is interesting to highlight that the synthesis protocol suggested by Kruk *et al.* for both silica nanotubes and hollow nanospheres, is very similar. These materials are obtained by using triblock copolymer (Pluronic F127) micellar systems as soft templates, in combination with a swelling agent (toluene, in this case). The only significantly different parameters in the two syntheses are the stirring speed and the time between the addition of a swelling agent and the silica precursor (tetraethyl orthosilicate, TEOS).^[1]

Certainly, gaining a thorough understanding of the mechanism behind the formation of hollow silica nanospheres and nanotubes is essential for the optimization, and tuning of their synthesis. Earlier research had proposed that hollow nanospheres are formed through the fragmentation of nanotubes. More recently, our research group definitively established that the crucial parameter determining whether tubular or spherical nanostructures form is the amount of surfactant-stabilized toluene present in the reaction mixture.^[3]

Nonetheless, a deeper understanding of the mechanism mentioned above is required. Herein, the synthesis of Sn-doped silica nanospheres is presented. The use of several NMR techniques is employed to understand more in-depth how the process of Pluronic F127 micelles formation is influenced by the toluene amount and the temperature, and how these parameters affect the formation of hollow nanospheres. Specifically, 1D and 2D NMR experiments have been acquired at different temperatures and toluene concentrations to obtain structural and dynamic information. Finally, the synthesized nanomaterials have been characterized through static and MAS solid-state NMR experiments of ²⁹Si and ¹¹⁹Sn.

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Development and Lewis Acidity of Pyramidal Triarylborane and Borenium Ions

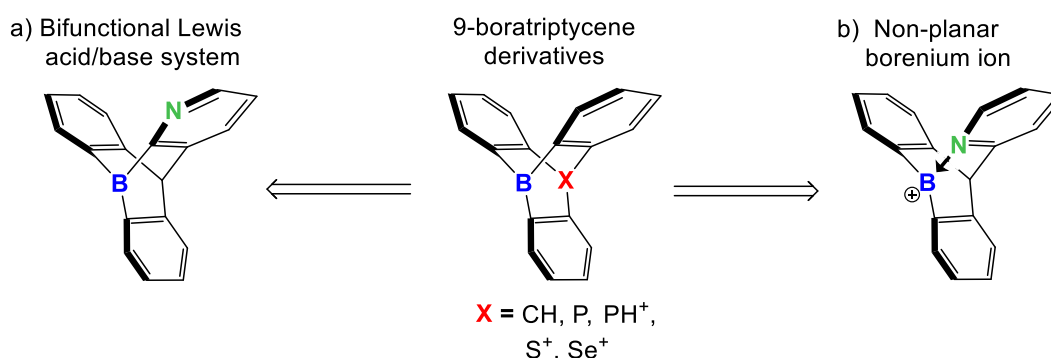
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Due to their unique chemical, physical and photophysical properties, organoboron compounds and in particular boron Lewis acids such triarylboranes are playing a central role in materials science, supramolecular chemistry, and catalysis.^[1]

Boron Lewis acids are usually planar trigonal species. However, constraining the boron atom in a pyramidal shape will significantly increase the Lewis acidity as demonstrated recently in our group with the synthesis and reactivity studies of 9-boratriptycene derivatives.^[2] It has recently been shown by quantum chemical calculations that incorporating an intramolecular Lewis base in 9-boratriptycene give access to a bifunctional boron/nitrogen system containing a pre-pyramidalized boron atom, the 9-bora-azatriptycene (Scheme 1a). It exhibits the potential to activate small molecules.^[3] On the other hand, borenium ions are increasingly used in organic synthesis for performing electrophilic borylations.^[4] Incorporation of a cationic boron atom in a pyramidal scaffold could lead to unprecedented structure and properties (Scheme 1b) and therefore increase their applications in chemistry.



Scheme 1 : Overview of this work, 9-bora-azatriptycene (a) and non-planar borenium ion (b).

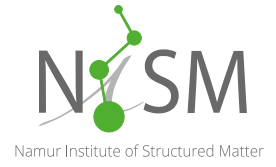
In this presentation, we will focus on the synthesis of the 9-bora-azatriptycene (Scheme 1a) and on a first prototype of pyramidal borenium ion (Scheme 1b) to obtain new types of Lewis superacids which are important in the field of frustrated Lewis pairs catalysis. Their Lewis acidity has been determined by quantum-chemical calculations in collaboration with the group of Pr. B. Champagne.

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Poster Abstracts

Exploring Reaction Mechanism of Diels-Alder Cycloadditions between Furan-Based Dienes and Ethylene Derivatives. A Study from the Perspective of Bond Evolution Theory

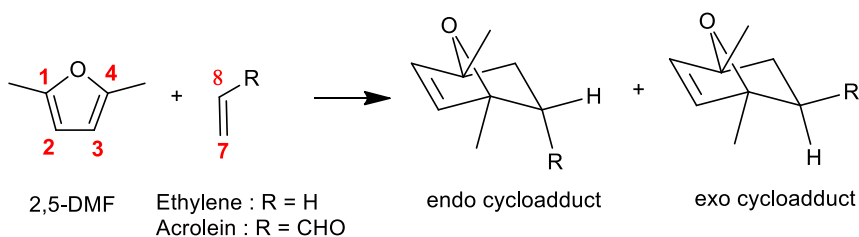
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The extensively studied [4+2] Diels-Alder (DA) reaction in organic chemistry is crucial for synthesizing hexagonal heterocycles and natural products. Involving a diene and a dienophile, it forms two new σ bonds, creating a carbocycle system. Numerous significant studies, combining experimental and computational methods like Density Functional Theory (DFT), focus on explaining the chemical bond formation and cleavage. Key objectives include understanding distinctions between concerted and stepwise pathways, as well as synchronous and asynchronous processes in the DA cycloaddition reaction mechanism. In light of this background, Krokidis et al. [1] have proposed the bond evolution theory (BET) which combines the electronic localization function (ELF) [2] and Thom's catastrophe theory (CT) [3] to unravel reaction mechanisms, which is the focus of our research work presented in this poster. In this work, with the aid of bond evolution theory, we examine at the M06-2X/6-311+G(d,p) level of theory the flow of electron density taking place along the [4+2] DA reactions between 2,5-dimethylfuran (2,5-DMF), derived from biomass and ethylene derivatives such as ethylene and acrolein (Scheme 1) [4].



Scheme 1. Schematic representation of the uncatalyzed DA reactions between 2,5-DMF and activated alkenes.

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Inverse opal material photocatalyst for enhanced light absorption facilitates photocatalytic conversion of renewable and low value biomass into value-added chemicals

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In the field of photocatalysis, three-dimensional ordered porous (inverse opal) photonic crystals have become photocatalyst structural candidates with great potential due to their special structure that enhances light absorption, mass transmission and diffusion efficiency compared to other structures.^[1] In the traditional photocatalytic hydrogen production process, it is often necessary to add sacrificial agents to consume holes, which makes the value of holes unable to be utilized.^[2] Therefore, it is imperative to look for low-value sacrificial agents and make full use of photogenerated holes.

Biomass, a most widely abundant and easily accessible natural resource have already supported mankind for thousands of years.^[3-4] Traditional thermochemical processes require high temperature and/or high pressure with intensive energy consumption for biomass conversion. Comparatively, photocatalytic biomass valorization provides the mild operation and high efficiency and selectivity.^[5-7] Biomass utilization by photocatalytic process the so called photoreforming is a novel concept and emerging technology.

In this talk, the inverse opal photocatalyst has excellent catalytic activity and can synergistically produce hydrogen in the photocatalytic conversion of biomass into high value-added chemicals. It opens up an economically sustainable path for biomass conversion.

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Surrounding effects on Raman optical activity signatures

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Cryptophane molecules are cage-like structures consisting in two hemispheres, each made of three benzene rings. These hemispheres are bound together with three $-\text{O}(\text{CH}_2)_n\text{O}-$ linkers of various lengths giving rise to a plethora of cryptophane derivatives. Moreover, they are able to encapsulate neutral guests: CH_2Cl_2 , CHCl_3 , ...; and charged species: Cs^+ , Tl^+ , ... Finally, they exhibit chiroptical properties thanks to the *anti* arrangement of the linkers between the hemispheres.

This work focuses on the Raman optical activity (ROA) signatures of Cryptophane-111 ($n = 1$ for each linker). More specifically, we aim at simulating accurately its ROA spectra with and without a xenon atom inside its cavity (Fig. 1). Experimental data (Buffeteau et al., 2017) have already demonstrated the effect of the encapsulation in the low-wavenumbers region. To generate the initial structures, we rely on the novel Conformer–Rotamer Ensemble Sampling Tool (CREST) program, developed by S. Grimme and co-workers. This is required due to the flexibility provided by the linkers. The CREST algorithm seems promising and has already been used to sample the potential energy surface (PES) of target systems before the simulation of their vibrational spectroscopies (Eikås et al., 2022).

We observe large similarities between the two sets of conformers (one with and one without Xe encapsulated), demonstrating the robustness of the CREST algorithm. For corresponding structures, the presence of xenon pushed the two hemispheres slightly further apart. After optimization at the DFT level, only one unique conformer has a Boltzmann population ratio greater than 1%, pointing out the relative rigidity of the cage. Based on this unique conformer, our simulations are in good agreement with the experimental data. Regarding xenon encapsulation, the (experimental and theoretical) ROA signatures at low wavenumbers are impacted: slight shifts in wavenumbers are observed as well as a decrease in relative ROA intensity for bands around 150 cm^{-1} . The wavenumber shifts were very well reproduced by our simulations, but the experimental decrease in the ROA intensity was unfortunately not reproduced.

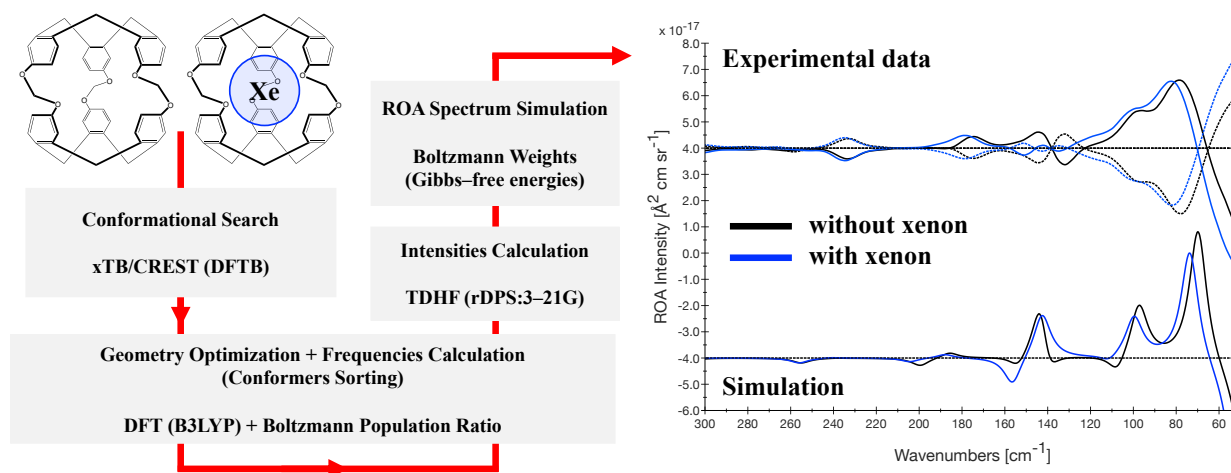


Fig. 1 – Methodology used in this work to simulate ROA spectra of cryptophanes.

Keywords: Raman Optical Activity (ROA) Spectroscopy, Computational Chemistry, Density Functional Theory, Conformational Search, Cryptophanes

Maximizing light outcoupling in OLEDs: insights from molecular simulations

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The efficiency of organic light-emitting diodes (OLEDs) is the product of internal quantum efficiency and a transmission factor of the light to go out of the device. While the internal quantum efficiency can reach 100% by material design and for instance relying on TADF materials; understanding how to maximize the transmission factor remains an open question and likely depends on several factors such as the molecular length and weight, the nature of the host materials and the glass transition temperature.

We investigate in a joint experimental-theory study the orientation of the c545t/coumarin 6 in several host materials. Experiments are carried out using single molecule microscopy^[1] in the OLED emissive layer where a c545t/coumarin 6 green emitter is dispersed in ultra-low concentrations (10⁻⁶ wt%) in different host material. This technique is able to show anisotropy behaviour by looking at the orientation distribution of individual emitter molecules in a system relevant to vacuum-processed devices. On the other hand, we perform corresponding multiscale simulations including molecular dynamics for the morphology of the film and quantum chemical calculations for the excited state properties. The forcefield methodology pathway focuses on reparameterization of a torsion dihedral angle with the Adapting Biasing Force (ABF) method to fit the quantum mechanical potential.

Several outlooks are planned with molecular dynamics simulations to simulate the vapor deposition on glass substrate and get the transition dipole moment aligned horizontally with respect to the plane of the device.

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Understanding the acidity properties of different silica-based materials via ^{31}P ssNMR using TMP as probe molecule.

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Nowadays, various industrial processes are performed with the aid of acid catalysts. In the past decades, Brønsted acids such as H_2SO_4 , H_3PO_4 and HF have been broadly used as homogeneous catalysts due to their acidic strengths. Despite their excellent catalytic performances, these homogeneous catalysts display serious drawbacks mainly related to equipment corrosion, difficult waste treatment and high toxicity. To solve the above-mentioned problems, solid heterogeneous acids such as zeolites, functionalized silica and supported heteropolyacids (HPAs) have been developed and largely employed in various catalytic chemical processes.¹ In general, the heterogeneous solid acids display two different kinds of acidity: Lewis (L) and Brønsted (B). Silica-based materials are among the most used heterogeneous catalysts due to their high specific surface area and pore size distribution. Moreover, the L/B acid balance can be tuned via the insertion of a metal cation in the structure or modifying the ratio between silicon and the selected metal cation. In this context, different analytical methods based on well known spectroscopic techniques have been developed with the aim to characterize these acidic features. Indeed, the overall acidity can be studied via the use of probe molecules (e.g. pyridine and ammonia) in combination with a temperature programmed desorption approach (TPD) or coupled to infrared spectroscopy (FT-IR).² Recently, it has emerged that detailed acid features such as nature, concentration, and strength of acid sites can be investigated by solid state nuclear magnetic resonance (ss NMR) selecting a suitable probe molecule containing NMR-sensitive nuclei such as ^{13}C , ^{15}N , or ^{31}P . Among all the possible probe molecules, trimethylphosphine (TMP) and trimethylphosphine oxide (TMPO) are largely employed in this field. The use of these two molecules is quite advantageous due to the wide chemical shift range of ^{31}P NMR allowing the clear identification of the different acid sites, and because ^{31}P is a dipolar nucleus with an abundance of 100%.³ Herein, we show the characterization of the L and B acidity of different silica-based materials using TMP as a probe molecule. Initially, a comparison between Hf, Ga and Sn silica hollow nanotubes is done. Afterward, Ga and Sn nanotubes are compared with the respective silica hollow nanospheres, to evidence a possible modification of the acid properties due to the different morphology of the solids. Finally, an oxidation treatment in air allows converting TMP into TMPO which can be employed to better understand the strength of the different acid sites.

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Structural and functional characterization of a copper efflux membrane protein: PcoB from *Caulobacter crescentus*

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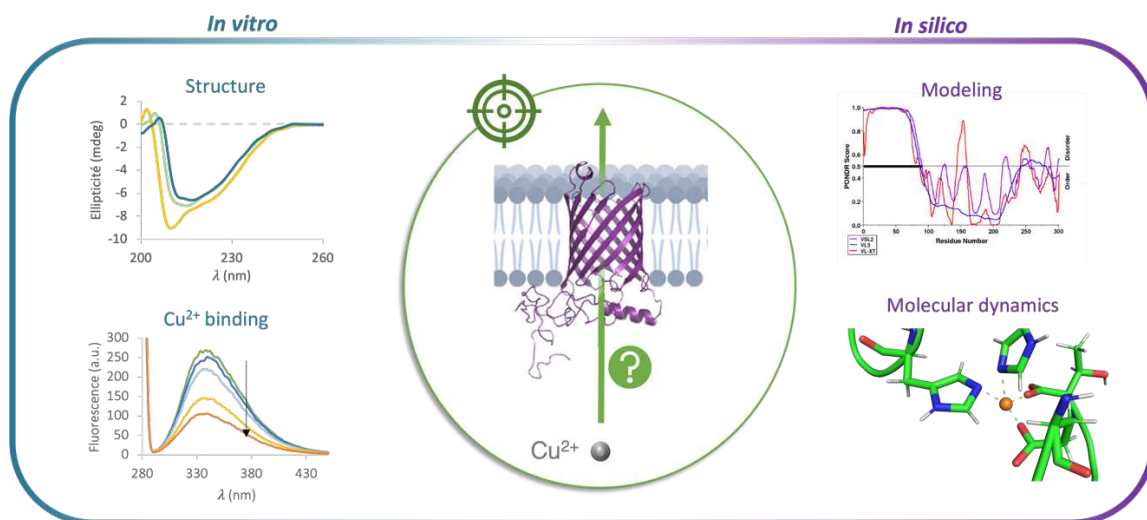
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Abstract

In recent years, the U.S. Environmental Protection Agency has classified copper as an antimicrobial agent due to its contact toxicity towards bacteria. This toxicity serves the aim of reducing hospital-acquired diseases.¹ However, some pathogenic bacteria, such as *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*, have developed the ability to resist to copper stresses through different copper regulation mechanisms. These species are all constituted of a system Pco, little studied except in *Caulobacter crescentus*, an aquatic α -proteobacterium, governed by a two-component system PcoAB. PcoA is defined in the literature as a multi-copper oxidase that converts Cu^+ to Cu^{2+} , while PcoB shaped by a β -barrel and a disordered chain, which is essentially unknown, is hypothesized to be responsible for the putative efflux of Cu^{2+} ions from the periplasm.^{2,3}

To confirm this hypothesis, the structures of the protein, its binding and selectivity to Cu^{2+} are studied using spectroscopic and calorimetric techniques, and are complemented by *in silico* studies (modeling and molecular dynamics). Furthermore, in order to highlight the role of the disordered N-terminal chain in copper cation transport, a mutant of the protein is also investigated in which this chain is truncated. Both proteins are overexpressed as inclusion bodies and then purified and refolded by various methods using detergent micelles.



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Investigation of the Antimicrobial Properties of Thin Films Produced by Low Pressure Magnetron

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Abstract:

The surfaces are transmission vectors of pathogens such as bacteria and viruses. By indirect contact mode between our hands and fomites, these microbes spread in our environment and contaminate us. That is all the more true in the hospitals where the immunosuppressed patients are most likely to contract infections. These latter are responsible for a significant part of morbidity and mortality worldwide, not only but also, a financier burden on our society.

The released-based plasma coatings are promising solution to this major problematic. The advantage of the release approach is to provide the anti-infectious agent locally, while avoiding any adverse toxic impact for human beings. Whatever the state it is in (ion, nanoparticles or colloids), silver (Ag) have known effects and it is used since the ancient times. Developed within the framework of nanomedicine, materials based on silver ion release have been among the most studied candidates for antimicrobial purposes.

In this work, we evaluate the possibility to produce antimicrobial, antibacterial and antiviral coating to be applied on any surfaces. Thin films (a-C:H:Ag) were produced by low pressure magnetron and deposited on stainless steel substrates. The colony-forming unit (CFU) method, LIVE/DEAD bacterial viability and modified 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 antiviral properties were evaluated by infectivity assays, Tissue Culture Infectious Dose 50% (TCID50) calculated by Reed-Muench Method and a quantitative colorimetric MTS assay based on the cytopathic effect (CPE). We used a Porcin Respiratory Coronavirus (PRCV), a virus of the *Coronaviridae* family that shares the same common features with SARS-Cov-2. The achieved results during this work show very promising antibacterial and antiviral activities. The mechanism of action of the silver-based coatings with a carbon matrix were investigated by X-Ray Photoelectron Spectrometry (XPS) and Scanning Electron Microscopy (SEM). The results obtained suggest a crucial role of silver segregation towards the surface and formation, of nanoparticle to explain the antimicrobial effect against bacteria and viruses. The data have been published [1].

Keywords: antibacterial coating, antiviral coating, silver, a-C:H, bacteria, virus, silver segregation

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Hierarchical Heterostructured Cathode for a Visible-Light-Involved in Lithium–Oxygen Battery

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Lithium-oxygen (Li-O₂) batteries are considered to be one of the most promising high-energy-density energy storage technologies. This is attributed to their high theoretical capacity (~1165 mAh g⁻¹) and energy densities (~3500 Wh kg⁻¹), which is at least an order of magnitude higher than that of commercial Li-ion batteries [1,2]. And the high theoretical capacity and energy density are a direct result of the redox reaction occurring between lithium ions and oxygen: 2Li + O₂ → Li₂O₂ (E⁰ = 2.96 V vs Li⁺/Li) [3]. Li-O₂ batteries operated through oxygen reduction reaction (ORR) during discharge process, and oxygen evolution reaction (OER) during charge process. For discharge product, the standard Gibbs reaction energy of Li₂O₂ is not only lower than that of Li₂O, but formation of Li₂O₂ also not requiring the cleavage of O-O bonds, whereas is requirement for Li₂O formation. As a result, Li₂O₂ as discharge product is both thermodynamically and kinetically favorable [4].

The electrical conductivity of Li₂O₂ is only about ~10⁻¹² to 10⁻¹³ S cm⁻¹, which is exceptionally low for conventional electronic conduction, causing sluggish ORR and OER kinetics and high reaction energy barrier, electrochemically exhibiting large overpotential (>1.0 V) and poor round-trip efficiency (<70%) [5,6]. Incorporating light energy into Li-O₂ batteries has been demonstrated as an effective way to lower the large voltage hysteresis. Herein, we report a heterostructured TiO₂/Co₃O₄ composite on carbon paper (TC/CC) as a bifunctional cathode catalyst, which has superior light harvesting capability and electron-hole separation rate, to facilitate ORR and OER for visible light-involved Li-O₂ battery.

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Tailoring short-chain sulfur molecules to drive redox dynamics for sulfur-based aqueous battery

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Sulfur is known to have a large number of allotropes, of which the most thermodynamically stable is the cyclic S_8 molecule. However, due to its relatively stable structure, cyclic S_8 molecule is unlikely to exhibit high electrochemical reactivity.^[1,2] Fortunately, cyclic S_8 molecule can decompose above the melting point and transform into different short-chain allotropes, mainly in the form of S_{2-4} .

Guided by thermo dynamics analysis, short-chain sulfur molecules (S_{2-4}) are successfully synthesized by space-limited domain principle. Unlike conventional cyclic S_8 molecules with complex routes in solid–solid reaction, short-chain sulfur molecules not only shorten the length of the redox chain but also inhibit the formation of irreversible intermediates, which brings excellent redox dynamics and reversibility.^[3,4] As a result, the Cu-S battery built by short-chain sulfur molecules can deliver a high reversible capacity of 3133 mAh g⁻¹.

Compared with cyclic S_8 molecules, short-chain S_{2-4} molecules facilitates the complete redox reaction of the sulfur cathode without producing electrochemically inert intermediates during the reaction process, which avoids the loss of sulfur species and enhances the cycling stability of aqueous Cu-S battery. Considering the convenience and economy of the synthesis process, the emergence of short-chain sulfur molecules can promote the development of high-performance sulfur-based aqueous batteries.

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Investigation of 1H-MoTe₂ doped with nitrogen

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Abstract:

Following the excellent studies on the molecular beam epitaxy (MBE) synthesis of high crystalline quality of MoTe₂ transition metal dichalcogenides (TMDs) materials with the observation of higher-indexed Moiré patterns in MoTe₂/graphene heterostructure (see figure) [1-4], we pursue further research on how to tune its electronic properties in a controlled way.

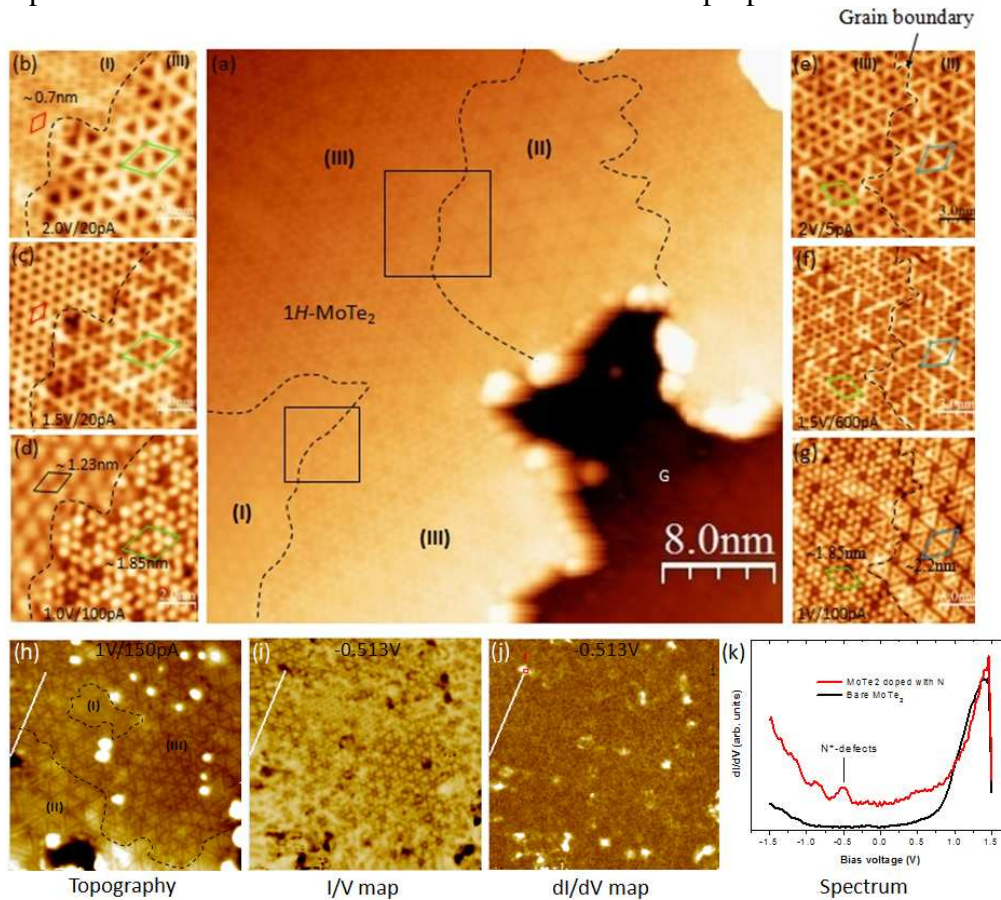


Figure: STM images of bare 1H-MoTe₂ on graphene/6H-SiC(0001): (a) 40×40 nm² area showing different surface structures of different Moiré patterns as marked by regions (I): $2\sqrt{3}R30^\circ$, (II): $\sqrt{3}R16.1^\circ$ and (III): $2\sqrt{7}R19.1^\circ$; (b) → (d) 10×10 nm² taken at the interface on a square between (I) and (III) with different bias voltages, (e) → (g) on an area between (II) and (III). (h) → (k) after doping with nitrogen, many bright spots and dark holes appear on the surface of MoTe₂. The bright dots on the dI/dV map are assigned to defects originating from nitrogen atoms in the MoTe₂ layer with a dominant peak detected at -0.5eV in the bandgap compared to bare MoTe₂. Figures (h-k) are not published yet.

To achieve this goal, doping is required and nitrogen is chosen for this purpose due to its interesting charge transfer through a physical substitution mechanism compared to chemical doping [5]. Although graphene doped with nitrogen (N*) produced by the remote RF plasma source has been demonstrated with the significant modifications of the electronic and

transport properties, the effect of nitrogen in other 2D materials such as MoTe₂ has remained largely unexplored. In this communication, we report experimental observations by low temperature STM/STS of two different types of defects generated by N* atoms. DFT calculations and simulations are underway to identify the nature of these defects.

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Exploring the electronic structure of extended triangulenes: opening new doors for a fast Reverse Intersystem Crossing

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The recent discovery of triangle-shaped compounds bearing an inverted S1-T1 energy gap (INVEST) has represented a promising strategy to harvest the triplet excitons and boost the Reverse Intersystem Crossing (RISC) process in fully organic molecular systems, allowing the enhancement of Organic Light Emitting Diodes (OLEDs) performances. In our previous works, we defined the computational protocol to describe these systems [1-3], entailing the employment of correlated wavefunction methods, and combining quantum-chemistry and group theory we related the optical properties of these molecules to their symmetry [4]. An intriguing design strategy emerging from these studies involved the extension of the molecular core by merging two INVEST units, resulting in a Uthrene-like structure. This leads to a non-zero oscillator strength of the S1 state, thus allowing emission of light, and concomitantly to the energy proximity of the two lowest singlet and triplet excited states, opening the door to multiple RISC channels which can pave the way for a new paradigm for the singlet-triplet conversion.

In this work, we select a series of Uthrene-like extended triangulenes, doped with nitrogen and boron atoms, and model their electronic structures employing correlated wavefunction methods such as SCS-CC2, NEVPT2 and EOM-CCSD. A closer look at the molecular orbitals and electron-correlation descriptors can help in the rationalization of the small energy gap between the two lowest singlet and triplet excited states. In addition, the computation of the non-radiative decay rates (ISC, RISC and internal conversion) can provide a first picture of the spin-conversion pathways occurring in the excited states, to identify the most promising candidate for next-generation OLED applications.

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Conversion of glycerol into solketal catalyzed by hybrid porous zirconium(IV) phosphonate networks

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Glycerol is one of the main by-products of the biodiesel industry and it is largely available in the market. From this versatile molecule, via an acetalization reaction it is possible to synthesize cyclic acetals, like solketal (Figure 1). The synthesis of solketal displays high atom economy and potential low E-factor.¹ Moreover, solketal can be used as green solvent and biofuel additive, eventually allowing industries to develop a circular economy. To enhance the conversion of glycerol into solketal, the use of an acid catalyst is needed. Both Lewis and Brønsted acidic sites are required to reach high efficiencies in catalysis.² In this work, a series of novel porous zirconium(IV) phosphonates as heterogeneous catalysts for the target reaction is proposed. These materials present a layered structure, where the zirconium(IV)-phosphate layers are interconnected via different spacers, namely phenyl diphosphonates and bi-phenyl diphosphates.³ The solids possess high specific surface area (e.g. from 300 to 400 m²/g) and they are stable until 300 °C.

From preliminary catalytic tests, it emerges that all the materials are very active towards the synthesis of solketal. Kinetic studies allowed determining the best conditions for the evaluation of the catalytic performances. One selected catalyst was employed as reference for further investigations. Hot filtration tests evidenced the absence of leaching of active sites occurs during the reaction. Moreover, the material preserved its activity for at least 5 consecutive cycles. Further catalytic investigations will be performed to determine the structure-activity correlation for the series of solids synthesized.

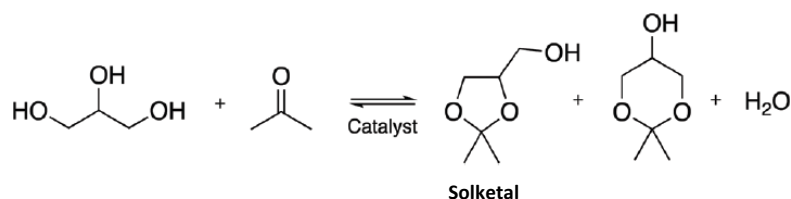


Figure 1. Conversion of glycerol into solketal.

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TOWARDS THE DEVELOPMENT OF COVALENT INHIBITORS FOR *BRUCELLA MELITENSIS* SERB THROUGH CRYSTALLOGRAPHY AND KINETICS

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Keywords: *Brucella melitensis*, Phosphoserine phosphatase, Inhibitors, Protein crystallization, Enzymatic assay.

Brucella melitensis is a pathogenic intracellular bacterium causing brucellosis, a chronic infectious disease affecting sheep and goat flocks. It can also affect humans after consumption of contaminated products or contact with infected animals.^{1,2} After studies carried out by Revora *et al* with an ortholog of *Brucella melitensis* (*Brucella abortus*, 99% sequence identity), it was shown that these bacteria cannot replicate without L-Serine and that the phosphoserine phosphatase enzyme is essential for the bacteria replication.³ Targeting this enzyme can therefore be a solution to decrease the bacteria propagation.

The main goal of the presented work is the inhibition of this enzyme with targeted covalent inhibitors (TCI) for the active site to prevent cellular replication. To this end, the first step is to find molecules with good affinity to the active site. Different substrate analogs were studied through enzymatic assays and X-ray crystallography (soaking and co-crystallization assays) to determine if they could be the starting point for the design of new TCI.

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Phosphonium Salt/Al-Porphyrin Copolymer as Bifunctional Heterogeneous Catalyst for CO₂ Conversion to Cyclic Carbonates

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The effective chemical valorization of CO₂ by means of its conversion into valuable products is now more than ever a topic of considerable interest.^[1] It is on that basis that herein, as a continuation of our ongoing research,^[2] we have chosen the conversion of CO₂ and epoxides to cyclic carbonates as a convenient route to achieve this goal.^[3] To catalyze this reaction, a new bifunctional heterogeneous material, composed of an aluminum porphyrin (Lewis acid) and phosphonium salts (nucleophile), called **TSP-AlCl-PhospBr** was designed. The prepared copolymer has been extensively characterized using various spectroscopic and analytical techniques. As a heterogeneous catalyst, it enables efficient chemical conversion of CO₂ and epoxides, even at low temperatures, down to 30°C, without the use of solvents. In particular, the catalyst demonstrates high turnover numbers (TON) and frequency values (TOF). The outstanding results were attributed to the close proximity of the two active sites, achieved by the direct covalent bond between the porphyrin ring and the phosphonium moieties, which allows them to cooperate in the activation and opening of the epoxide ring (**Figure 1**). Moreover, recyclability studies on **TSP-AlCl-PhospBr** have shown its stability and reusability for consecutive cycles without the need of reactivation procedures.

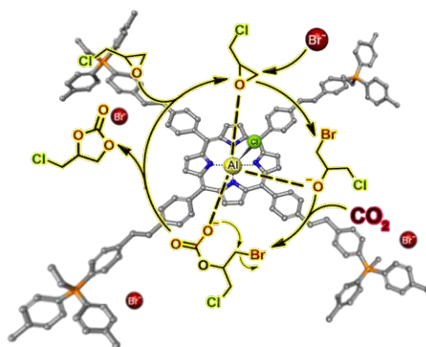


Figure 1 : Representation of the synergy between Al-porphyrin and phosphonium salt in the synthesis of cyclic carbonates.

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Synthesis of Hierarchical Single-Crystal ZSM-5 and SAPO-34 Zeolite

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As a size- and shape-selective catalyst, zeolites are widely used in petroleum and fine-chemicals processing. However, their small micropores severely hinder molecular diffusion and are sensitive to coke formation. Hierarchically porous zeolite single crystals with fully interconnected, ordered, and tunable multimodal porosity at macro-, meso-, and micro length scale, like in leaves, offer the ideal solution. However, their synthesis remains highly challenging.

Here, we report a versatile confined zeolite crystallization process to achieve these superior properties.^{[1][2]} zeolite single crystals lead to significantly improved mass transport properties by shortening the diffusion length while maintaining shape-selective properties, endowing them with a high efficiency of zeolite crystals, enhanced catalytic activities and lifetime, highly reduced coke formation, and reduced deactivation rate in bulky-molecule reactions and methanol-to-olefins process. Their industrial utilization can lead to the design of innovative and intensified reactors and processes with highly enhanced efficiency and minimum energy consumption.

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Sharing Electronic and Ion Transfer Channels by In-Situ Integration of Gel Polymer Electrolyte for Solid-State Lithium-Oxygen Battery

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Construction of three-phase boundaries (TPBs) is a recurring theme in lithium-oxygen batteries (LOBs), especially in light of the emergence of thick cathodes.^[1,2] Herein, we adopt a gel polymer electrolyte (GPE) to create integrated cathodes for LOBs that construct ionic and electronic dual transfer channels and offer auxiliary structural support for the fragile cathode skeleton. Such materials essentially resolve the mass transfer issues in LOBs and successfully build substantial TPBs throughout the entire thick cathode (~2 mm), resulting in exceptional performances with an areal specific capacity of 22 mAh cm⁻² and a gravimetric specific capacity of 19000 mAh g⁻¹ calculated based on the cathode's total weight. A numerical model is introduced to provide insight on dynamics evolution,^[3] theoretically verifying the reasonableness of the integrated design. Besides, how well batteries would perform with GPE improvements is predicted, indicating their vast prospects for utilization. The present work demonstrates our revolutionary integration strategy proffers an elegant solution to fragile 3D cathodes, which shows their potential in energy storage devices.^[4,5]

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Impact of Mo/W distribution on the properties of Keggin catalysts

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The drive to develop environmentally friendly chemical processes has motivated a significant increase in research activities that encompass understanding and designing phosphotungstic and phosphomolybdic acids catalysts.^[1,2] Due to their high activity in acid-catalyzed reactions, tungstophosphoric acid is a potential replacement for corrosive and environmentally toxic acid catalysts currently. The acid strength of phosphotungstic acid, which is potential indicators of solid acid activity study in many researches.

In this work, we studied the general systems $[PW_{12-m}Mo_mO_{40}]^{3-}$ with $m= 0-12$ as Keggin catalysts. The total of 182 different systems are identified by our home-made program according to the symmetry of Keggin catalyst $[PW_{12}O_{40}]^{3-}$.^[3] Density functional theory (DFT) calculations are performed to explore to the optimal number and positions of Mo and W atoms in Keggin catalysts to maximize the acid strength. The different descriptors are employed such as proton affinity, charge distribution and O core orbital (1s) energies. In the current result, it indicates that the most energetically favorable site of the acidic proton to be a bridging oxygen atom in the anhydrous heteropolyacid.

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Non-covalently synthesis of porous organic salts

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The preceding years have experienced the booming development of porous materials in a wide range of fields, from the inorganic skeleton of zeolites, activated carbon, silica, to hybrid metal–organic frameworks (MOFs), covalent organic frameworks (COFs), conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), and porous aromatic frameworks (PAFs). Although these porous materials exhibit advantages in scientific fields, porous materials with rigid structure and permanent porosity have been rarely reported. Porous organic salts (POSs) are a new member of porous materials and constructed by ionic bonding and hydrogen bonding between organic acid and base. Because of the special ionic bond, POSs provide the confined channels for transportation of high polar molecules which makes them distinct from other porous organic materials (POMs). Aside from that, POSs possess permanent porosity that means voids show long-term stability and reversibly accessibility after removing guest molecules. Generally, permanent porosity correlated closely with the strength of ionic bonding and rigidity of framework. However, it is worth noting that ionic bond is non-directional, which makes the joint of framework too flexible to sustain high intermolecular free volume. Hydrogen bond is a powerful intermolecular force and more importantly, it is directional which can deteriorate flexibility resulting from non-directional ionic bond. The POSs with high polarity channel and new promising applications have become a new family of porous organic frameworks¹.

In this work, POS-1 was successfully synthesized using 1,4-benzenedisulfonic acid and 2,7,15-triaminotriptycene. The single crystals were crystallized in methanol solution. The single crystal X-ray diffraction results revealed that POS-1 exhibits monoclinic crystal system with space group of *C2/c*. The lattice parameters of $a = 13.31 \text{ \AA}$, $b = 18.62 \text{ \AA}$, $c = 29.72 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$, $\beta = 96.73^\circ$. There is 1D pore channel along *a* axis. The volume of the void space is 14% with the space of $10.5 \times 10.5 \text{ \AA}$. The asymmetric unit is composed of one 2,7,15-triaminotriptycene and $3/2$ 1,4-benzenedisulfonic acid and $7/2$ water molecules. Because of the asymmetric position of amino group in triptycene, there are torsion in the unit cell. The 1,4-benzenedisulfonic acid and 2,7,15-triaminotriptycene extend along *a*, *b* and *c* axis with an angle. The molecules connect to three-dimensional network through hydrogen bonds. The CH- π interaction exist when densely packing. There is no defined supramolecular cluster because the length of benzene and triptycene is not well matched. And also, aside from the charge-assisted hydrogen bond between sulfonate group and amino group, there is neutral hydrogen bond between water molecule, sulfonate group and amino group.

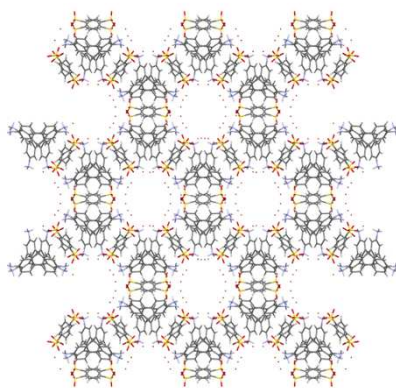


Figure 1. The packing diagram of POS-1. (C: gray; N: blue; O: red; S: yellow; H: white).

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Integrated insights into NH_4^+ storage mechanism and electrochemical kinetics of ultrastable Prussian blue analogues for Ammonium-Ion Battery

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Ammonium-ion batteries (AIBs) have recently attracted increasing attention in the field of aqueous batteries owing to their high safety and fast diffusion kinetics.^[1-4] The NH_4^+ storage mechanism is quite different from that of spherical metal ions (e.g. Li^+ , Na^+ , K^+ , Mg^{2+} , and Zn^{2+}) because of the formation of hydrogen bonds between NH_4^+ and host materials. As one of the main host materials, PBAs with 3D channels have been extensively investigated in AIBs.^[5] The formula for PBAs can be roughly expressed as $\text{A}_x\text{M}_m[\text{M}_n(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$, where A represents the cation (e.g. Na and K) for charge compensation, M_m and M_n stand for transition-metal ions (e.g. Cu, Ni), respectively. m, n, x, and y are their stoichiometric values. The size of the channels in PBAs is about 0.32×0.32 nm, which is larger than the ionic radius of NH_4^+ (0.154 nm). In this work, the NH_4^+ storage mechanism during the charging/discharging process is investigated. In addition, hydrogen bonds are formed between the hydrogen atom in NH_4^+ and nitrogen atom in PBAs framework during the NH_4^+ insertion process, which is beneficial for electrochemical and structural stability.

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