DEVELOPMENT OF 2D-2D HETEROSTRUCTURES OF MOF DERIVED CO_3O_4 NANOSHEETS AND g-C_3N_4 FOR CO_2 PHOTOREDUCTION

Maria Anagnostopoulou [1], **Thomas Cottineau** [1], **Valérie Keller** [1], **Konstantinos C. Christoforidis** [1,2]

[1]Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, Université de Strasbourg, Strasbourg, France;
[2]Department of Environmental Engineering, Democritus University ofThrace, Xanthi, Greece;
(Corresponding author: kochristo@env.duth.gr)

ABSTRACT:

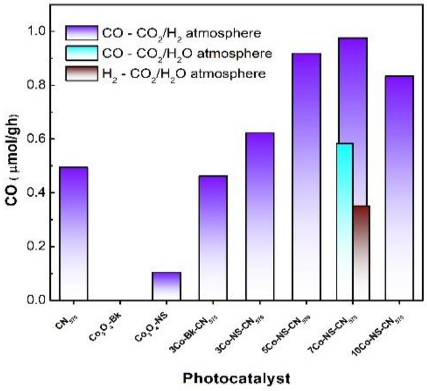
Climate change and energy crisis are imposing the utilization of clean and renewable energy systems [1]. Solar fuels produced via photocatalytic pathways are a promising alternative to fossil fuels. In this direction, the development of appropriate, non-toxic and cost-effective materials that can be used as photocatalysts is highly important.

Herein, we present the case of carbon nitride functionalized with Co_3O_4 of different morphologies (nanosheets (NS) and bulk (Bk)). CN has been synthesized by melamine poly-condensation and was post-modified by a facile thermal treatment at different temperatures. For the development of the heterostructures, MOFs (ZIF-67 and modified-ZIF-67) are used as templates for Co_3O_4, and they are combined in different percentages with the pre-formed CN. Oxides are developed in situ on the surface of CN after calcination. The utilization of MOFs allows the control of Co_3O_4morphology.

The Individual materials and the composites are characterized for their structural, optical and electronic properties. Specifically, SEM and TEM verified that the morphology of Co_3O_4 may be controlled (Bk vs. NS) by the MOF structure used as precursor. Concerning the optical properties, CN samples exhibit an absorbance onset at ca. 450 nm, while all composites present light absorption in the whole visible region, attributed to the Co_3O_4. Surface area analysis shows that the thermal exfoliation and the presence of Co_3O_4 ameliorate the available total area. XPS characterization showed that Co_3O_4-NS possesses more abundant oxygen vacancies in comparison with Co_3O_4-Bk.According to EPR and photocurrent results, it is suggested that formation of photo-generated electrons is enhanced in the case of the 2D-2D heterostructure.

Concerning their photocatalytic performance, all composites show higher activity than their individual counterparts (Fig. 1). Noteworthy, the composites bearing Co_3O_4-Bk presented lower activity than the 2D-2D heterostructures. Supplementary experiments of CO_2 photoreduction, with H_2O as the reducing agent, were carried out for the most active photocatalyst, showing good selectivity towards CO formation over H_2.

Figure 1: CO_2 Photocatalytic reduction results



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High pressure intrusion of non-wetting liquid in hydrophobic Zeolitic Imidazolate Frameworks for mechanical energy storage/absorption

Amir Astafan[1,2], Andrey Ryzhikov[1,2], Habiba Nouali[1,2], T. Jean Daou[1,2], Claire Marichal[1,2], Gérald Chaplais[1,2]

[1] Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, Axe Matériaux à Porosité Contrôlée (MPC), F-68100, Mulhouse, France ;

[2] Université de Strasbourg, F-67000 Strasbourg, France
(Amir Astafan : amir.astafan@uha.fr)

ABSTRACT:

Heterogeneous lyophobic systems (HLS), which combine a lyophobic porous matrix and a non-wetting liquid, are one of the promising technologies to absorb and store the mechanical energy [1-4]. Depending on various physicochemical and structural parameters related to porous material combined with the nature of non-wetting liquid, HLS is able to restore, dissipate or absorb the mechanical energy supplied during the intrusion step and therefore to display a spring, shock-absorber or bumper behavior. In 2013, our team paved the way for the use of hydrophobic Zeolitic Imidazolate Frameworks (ZIFs) as porous matrix for HLS by studying “ZIF-8−water” system [2]. Since then, the energetic performance of others ZIFs-based HLS have been studied. The use of aqueous salt solutions as non-wetting liquid has been found as a way to improve energetic performance of HLS by the increase of intrusion pressure and the change of their behavior in some cases [3-4]. In this work, the influence of anion and cation nature on the energetic performances of “ZIF-8–aqueous salt solution” systems are studied on the example of potassium halides and alkali metal chlorides.

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Development of 3D scaffolds for tissue engineering

Quentin Bailleul[1], **Dominique Collin**[1], **Mehdi Vahdati**[1], **Damien Favier**[1], **Pierre Schaaf**[2], **Fouzia Boulmedais**[1‡]

[1] University of Strasbourg, CNRS, Institut Charles Sadron, France ;
[2] INSERM UMR_S 1121, Biomaterials and Bioengineering, University of Strasbourg, France
‡ (corresponding author: fouzia.boulmedais@ics-cnrs.unistra.fr)

ABSTRACT:

With the aging of population and affliction coming as consequences, replacement of organs and biomedical implants is of first importance. The development of biomaterials for this purpose is an important subject of research. Biomaterials are evolving from being bioinert to bioactive, meaning that that play a direct role in their integration/inclusion in the body. The control of the structure [1,2], conductivity [3,4] and mechanical properties [5] is very important, as they are some of the key parameters for cell differentiation (Fig. 1a). CoPEC (Compact PolyElectrolyte Complexes) are formulated by polyelectrolytes of opposite charges at high concentration in polymer and salt and formed through ultracentrifugation [6] or drop-casting. They can have mechanical properties close to biological tissues, important for a better integration and be made from biocompatible polysaccharides, such as chitosan and alginate [7].

In this study, we developed a simple method to obtain PSS/PDADMA (poly(styrene sulfonate)/poly(diallyldimethyl ammonium)) CoPEC materials by a simple change of solvent focusing on their characterization depending on the polymers molecular weight (M_w). The porosity of the materials has been studied using fluorescent confocal microscope along with their mechanical properties using a rheometer and tensile test machine. The size and distribution of the pores increase with the $M_{w,}$ with a mean size between 5 and 50 µm. The mechanical properties of the materials evolve from a brittle behavior at low M_w to a stretchable property at high M_w.

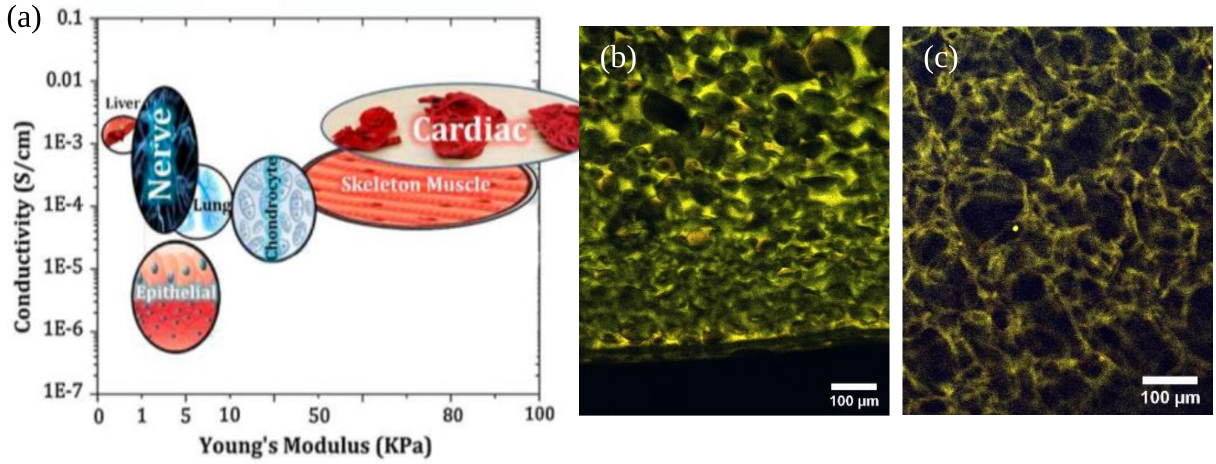

Figure 1 **: (a)** Conductivity and young modulus values of different biological tissues **[8]**
(b) confocal microscopy picture of an average M_w CoPEC and **(c)** of a high M_w CoPEC

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DEEP-UV LITHOGRAPHY OF NANOCOMPOSITE THIN FILMS INTO MAGNETOOPTICAL GRATINGS WITH NANOMETRIC PERIODICITY

D. Berling[1,2]*, C. Bidaud[1,2], D. Jamon[3], E. Gamet[3], F. Royer[3], S. Neveu[4], O. Soppera[1,2]

1. Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France
2. Université de Strasbourg, France
3. Université de Lyon, CNRS, UMR 5516, Laboratoire Hubert Curien, Université Jean-Monnet, 18 rue Pr. Lauras, F-42000 Saint-Etienne, France
4. Sorbonne Université, CNRS, Laboratoire de Physicochimie des Electrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France
(dominique.berling@uha.fr)

ABSTRACT:

Non-reciprocal magneto-optical (MO) devices are essential components for the development of innovative integrated devices in telecommunication technologies or sensing applications. However, actual MO materials require multi-steps processes at high temperature which impedes a direct integration as optical components in complex systems. Thanks to its formulation flexibility, the sol-gel chemistry is a powerful way to develop new functional materials. In this work, we prepared a MO material, based on a sol-gel matrix doped with magnetic nanoparticles (MNP). [1,2]

The sol gel matrix is prepared from inorganic precursors. Titanium acts as photoinitiator under Deep UV irradiation (DUV) [3]. The first challenge of this composite approach lies in the incorporation of crystalized MNP in the photostructurable host matrix in a randomly dispersed regime, and the avoider of any aggregation. The MNP has been chosen to exhibit good MO properties: at a 1.5 µm wavelength the cobalt ferrite $CoFe_2O_4$ NP present an enhanced Faraday rotation, which is the MO effect expected here.

Moreover, this MNP doped matrix has been nanostructured (500 nm periodicity) through direct Deep UV laser writing process. The preparation of such structures with a sub-micrometric period hence does not necessitate any curing, which is coherent with the integration of this MO optical material in complex optical devices.

The combination of the intrinsic MO effect of the MNP with a nanostructure allowed us to obtain a good Faraday rotation: those structured thin films turn out to be excellent candidates to be used as a MO qualified material. [4] A demonstrator of a Faraday rotator has been prepared, which consists in this nanostructured hybrid material deposited on a waveguide, with properties that are comparable to the devices commercially available [5].

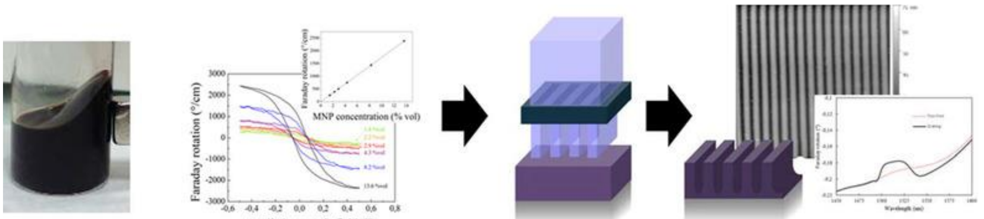

Figure 1: The photosensitive hybrid sol-gel matrix with $CoFe_2O_4$ MNPs, to obtain a hybrid magneto-optical nanocomposite film doped by up to 20%vol with NPs that can be photostructured using lithography methods to obtain a submicrometer periods MO gratings.

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Albupad project: Protein based biomaterials for the delivery of anti-tumoral active ingredients

Jordan Beurton [1], **Eya Aloui** [1], **Philippe Lavalle** [2], **Benoit Frisch** [1]

1.*Laboratory of Design and Application of Bioactive Molecules (CAMB) – Biovectorisation - UMR 7199, University of Strasbourg, France*

2. Biomaterials and BioEngineering - Inserm UMR_S 1121, University of Strasbourg, France

Corresponding author: jbeurton@unistra.fr

ABSTRACT:

The Albupad project is about the development of protein based biomaterials showing plastic behaviors and tunable features (shape, size, porosity…). These materials are obtained through the salt assisted compaction of albumin. They can be loaded with active ingredients to create implantable devices for a drug delivery purpose. The Albupad materials can outperform and replace synthetic implantable polymers by providing a higher biocompatibility and an easier green production process.

The biocompatibility of unloaded human albumin-based implants has already been demonstrated *in vivo*, in a humanized mouse model. The study presented here focuses on the adaptation of the Albupad technology for the delivery of anti-tumor molecules. Doxorubicin, a DNA intercalant, is a highly suitable active ingredient for this type of application [1]. Indeed, this molecule represents a reference treatment for several types of cancer such as breast or esophagus cancer. However, this active principle generates a strong systemic toxicity and suffers from a lack of specificity [2]. Thus, the development of localized delivery systems would reduce the risks related to doxorubin and increase the efficiency of these treatments. Doxorubicin loaded materials were formulated and characterized. The release kinetics of doxorubicin was studied as a function of its loading rate and the material formulation process. Two different delivery profiles were identified, one with moderate flux and long-term release (>30 days) and the other with a higher flux and shorter release time (≈ 30 days). The study of direct and indirect cytotoxicity of doxorubicin-loaded materials was performed on two human cancerous cells strains (HCT-116 and MCF-7). The efficiency of the materials was found similar to the one of free doxorubicin, demonstrating that the release of active doxorubicin is allowed by our system.

Finally, an *in vivo* study aiming to demonstrate the therapeutic efficiency of peri-tumoral implants is underway on a mouse model with orthotopic tumors.

Keywords: drug delivery, albumin, implantable device.

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Interpenetrating polymer network hydrogels using natural based dyes initiating systems: Antibacterial activity and 3D/4D performance

Hong Chen 1,2, Christophe Regeard 3, Hanène Salmi 4, Fabrice Morlet-Savary 1,2, Nicolas Giacoletto 5, Malek Nechab 5, Pu Xiao 6*, Frédéric Dumur 5*, Jacques Lalevée 1,2*

1 Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France.

2 Université de Strasbourg, F-67200 Strasbourg, France

3 Université Paris-Saclay, CNRS- CEA, I2BC, 91198 Gif sur Yvette, France

4 Université Paris-Saclay, CNRS, ICMMO- SM2ViE UMR 8182, 91405 Orsay cedex, France.

5 Aix Marseille Université, CNRS, ICR UMR 7273, F-13397 Marseille, France.

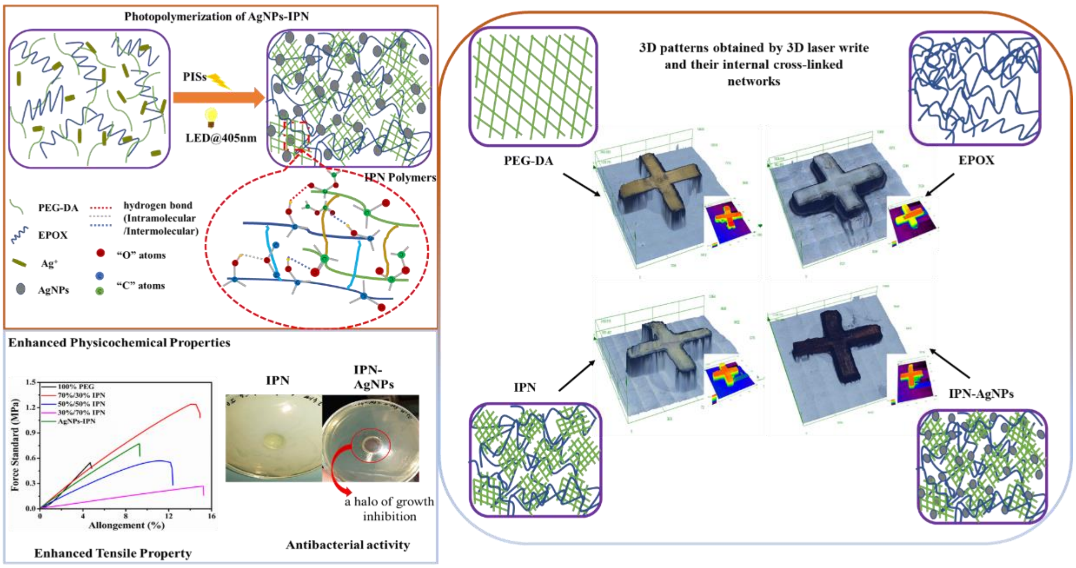
6 Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

** Corresponding author: jacques.lalevee@uha.fr (J. L.), frederic.dumur@univ-amu.fr (F.D.); pu.xiao@anu.edu.au (P. X.).*

ABSTRACT:

In the past few decades, interpenetrating polymer network (IPN) hydrogels have attracted huge attention due to their special cell-like structures, interpenetrating interface, and two-phase continuity, which has special synergistic effects on their performance and function [1-2]. In this work, eleven different dyes based on 1-aryl-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one or 3-aryl-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one were firstly synthesized, and combined with an amine (i.e. ethyl l,4-(dimethylamino)benzoate, EDB) and an iodonium salt (bis(4-tert-butyl phenyl) iodonium hexafluorophosphate, Iod) as the three-component photoinitiating systems (PISs) to induce both the free radical photopolymerization (FRP) of polyethylene glycol diacrylate (PEG-DA) and the cationic photopolymerization (CP) of 3,4-epoxycyclohexylmethyl-3’,4’-epoxy-cyclohexane carboxylate (EPOX) under the irradiation of LED@405nm. The best candidates were selected from the proposed eleven different dyes to study the relevant oxidation-reduction reaction mechanisms through various techniques. The best candidates were also used to prepare PEG-DA/EPOX interpenetrating polymer networks (IPNs). More interestingly, stable 3D patterns were successfully produced through direct laser write (DLW) technology, meanwhile, the silver cations could also be reduced in situ into silver nanoparticles. Furthermore, 4D printing could be achieved since all the obtained 3D patterns exhibited reversible swelling properties and the shape-memory effect caused by swelling and dehydration processes. Parallel to this, the influence of AgNPs on the mechanical properties of the 3D-printed objects and on IPNs was also systematically studied. Finally, the obtained IPN polymers containing silver nanoparticles (AgNPs) exhibited antibacterial activities for Gram-positive bacteria (e.g. Staphylococcus aureus) and Gram-negative bacteria (e.g. Pseudomonas aeruginosa).

Figure 1 : The photopolymerization of AgNPs contained IPN polymers and their antibacterial activity and 3D application.



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Consortium Strasbourgeois en Opto-Électronique Organique.

Organic Opto-Electronics Consortium Strasbourg

Laure Biniek [1], Martin Brinkmann [1], Yves André Chapuis [3], Anthony D'Aléo [2], Sadiara Fall [3], Anne Hébraud [4], Benoit Heinrich [2], Thomas Heiser [3], Loic Mager [2], Nicolas Leclerc [4], Patrick Lévêque[3], Yaochen lin [3], Evelyne Martin [3], Stéphane Méry [3], Emilie Steveler [3], Amparo Ruiz-Carretero [1], Gilles Ulrich [4].

[1] Institute Charles Sadron (ICS), SYCOMOR, Strasbourg, France.
[2] Institut de Physique, Chimie et Matériaux de Strabsourg (IPCMS), Département des matériaux Organiques, Strasbourg, France.
[3] Laboratoire des sciences de l'ingénieur, de l'informatique et de l'imagerie (ICube), MaCEPV, Strasbourg, France.
[4] Institut de chimie et procédés pour l'énergie, l'environnement et la santé (ICPEES), Strasbourg, France.

ABSTRACT:

The consortium, founded in 2010, aims to bring together Strasbourg's actors in the field of organic electronics, gathering members from four research institutes located on the Cronenbourg campus: ICPEES, ICS, IPCMS and ICube.

The consortium, which currently comprises 17 permanent researchers and lecturers, promotes interaction and common understanding between the different disciplines involved in organic opto-electronics, from molecular chemistry to device elaboration and including advanced structural and opto-electronic characterizations. Since its creation, the consortium has carried out projects in several areas of organic optoelectronics including lighting (organic electroluminescent diodes and LASERs), energy production (organic photovoltaic devices, organic thermoelectrics), smart windows (photovoltaic spatial light modulators) and health (bio-imaging, organic electrochemical transistors).
The members of the consortium also participate in the training of young researchers, by funding master's, doctoral and post-doctoral fellowships in chemistry, physical chemistry and physics.
The two posters presented at this HiFunMat conference illustrate the activities of the consortium through some examples of work carried out.

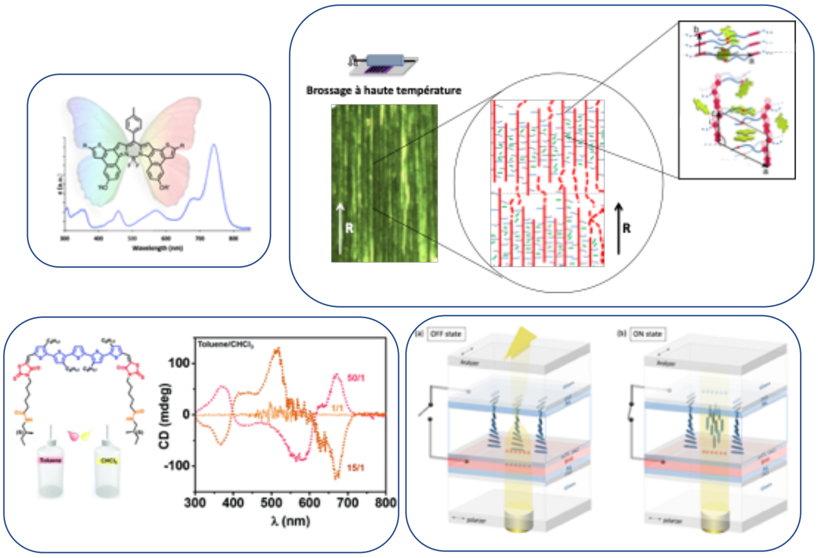

Figure 1. Illustration of research activities carried out by the concortium

Pentagonal gold bipyramids self-assemble with long-range triclinic order

Jieli Lyu,[1] Wajdi Chaabani,[1] Evgeny Modin,[2] Andrey Chuvilin,[2,3] Thomas Bizien,[4] Frank Smallenburg,[1] Marianne Impéror-Clerc,[1] Doru Constantin,[5] Cyrille Hamon[1]

[1] Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France;
[2] Electron Microscopy Laboratory, CIC NanoGUNE BRTA, 20019 Donostia – San Sebastian, Spain;
[3] Basque Foundation of Science, IKERBASQUE, 48013 Bilbao, Spain;
[4] SWING beamline, SOLEIL Synchrotron, Gif-sur-Yvette, France;
[5] Institut Charles Sadron, CNRS and Université de Strasbourg, 67034 Strasbourg, France;
constantin@unistra.fr

ABSTRACT:

The packing of solid bodies is one of the oldest problems in the natural sciences. Among the various shapes, spindles (elongated objects with two sharp tips) yield a surprising variety of arrangements, depending on their cross-section. We elucidate for the first time the three-dimensional stacking of spindle-shaped objects, experimentally and via simulations, by focusing on bipyramids of regular polygonal base with *n* sides. For *n* = 5 the crystal symmetry is triclinic, with lower symmetry than the building blocks of the structure and with two particles per unit cell. Further simulations confirm that these features are present for other odd *n* values: they can be attributed to the non-centrosymmetric shape of the particles. Surprisingly, this symmetry reduction is accompanied by a lower packing fraction than in the even *n* case [1].

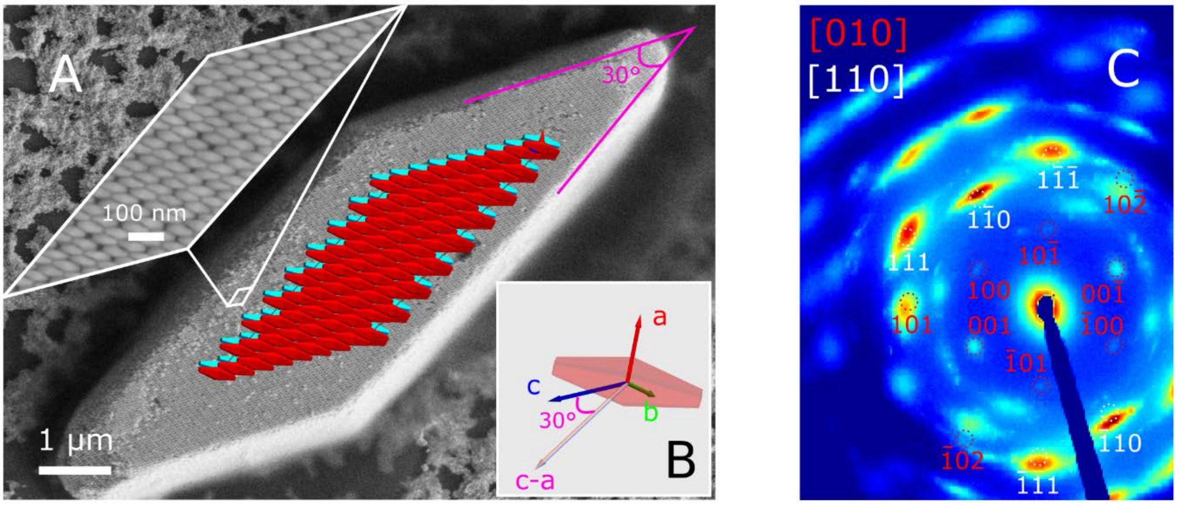

Figure 1: A) SEM image of one supercrystal, with superimposed model (the unit cell contains one red and one blue particle, rotated by 2π/5 with respect to each other). Inset: magnified image of the supercrystal surface. B) Unit cell of the model oriented along the c and c-a vectors of the triclinic lattice. C) 2D SAXS image (in log intensity scale). The Miller indices corresponding to the triclinic lattice are indicated on some Bragg spots. Two colors (red and white) are used for the indexation of two supercrystals with different orientation defined by the corresponding zone axis [UVW].

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ProBioTion project: towards the formation of protein bioplastics using ionizing radiations

Catherine Galindo[1], Antoine Danvin[1], Nicolas Ludwig[2], Arnaud Ponche[3], Philippe Peaupardin[1], Florent Kuntz[2], Quentin Raffy [1]

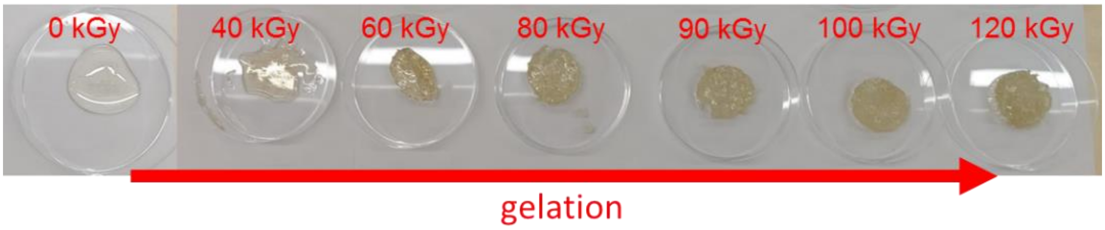
[1] IPHC, UMR 7178, 23 Rue du Loess, 67200 Strasbourg, France
[2] Aerial-CRT, 250 Rue Laurent Fries, 67400 Illkirch-Graffenstaden, France
[3] IS2M, CNRS-UHA UMR 7361, 15 rue Jean Starcky 68057 Mulhouse, France
corresponding author: caherine.galindo@iphc.cnrs.fr

ABSTRACT:

The valorization of bioresources is an environmentally friendly alternative for substituting crude oil-based plastics. Proteins are promising candidates for the production of biomaterials due to their thermoplastic properties, biodegradability and structural diversity. Teams of IPHC, IS2M and Aerial are combining their expertise to develop self-supporting protein films, and protein-functionalized materials, by irradiation. Ionizing radiation (10 MeV electrons at Aerial and proton beams) are used to ensure the cohesive structure of the films, avoiding the addition of crosslinking agent. Composite materials will be developed based on polymers functionalized at their surface by proteins presenting enzymatic activity, which will be coupled by radiolysis.
The thermomechanical properties of the materials, the degree of crosslinking and the enzymatic activity of the proteins will be evaluated.

When exposed to 10 MeV electrons beams, at doses above 50kGy, aqueous solutions of 30% w/w Bovine Serum Albumin (BSA) were converted into insoluble gels (**Figure 1**). Increasing dose resulted in a rise of the gelation rate (determined by HPLC and gravimetric measurements) and a concomitant decrease of the swelling of the gel. The secondary structure of the protein was affected with a slight conversion of alpha helices into beta structures at doses above 80kGy. In contrast, under identical conditions, lysozyme, an enzyme, gave rise to hydrosoluble gels, in which the protein retains its native conformation.
First results with 2 MeV accelerated protons will also be presented.

Figure1 : Evolution with the dose of the aspect of a 30% w/w BSA solution under irradiation by 10 MeV electrons



CHIRAL STIMULI-RESPONSIVE METALLO-SUPRAMOLECULAR ASSEMBLY INDUCED BY CUII/CUI REDOX CHANGE

Caitlyn Dussart [1], Maya Marinova, Antoine Bonnefont [2], Thierry Achard [1], Aline Maisse-François [1] , Stépahen Bellemin-Laponnaz [1]

[1] Institut de physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg, France,
[2] Institut de Chimie de Strasbourg, UMR 7177, Strasbourg, France
caitlyn.dussart@ipcms.unistra.fr

Keywords: coordination chemistry, cyclic voltammetry, copper complexes, chirality, metallopolymers

Texte:

Metallo-supramolecular polymeric assemblies are a new class of materials that has emerged in the last few decades.[1] These materials have a large range of properties depending on the nature of the metal centers and their ditopics ligands. The reversibility of their linkages can be used to do a supramolecular chiral recognition between enantiomeric molecules. This ability can lead to self-discrimination or self-recognition and generate pairs of enantiomers that are homochiral or heterochiral complexes.[2]

Our recent advances in this field will be presented.[3] We will describe how the Cu^I/Cu^{II} redox transition shows a chiral self-recognition or a self-discrimination through electrochemical studies. This phenomenon is also observed with the metallo-supramolecular copolymers, based on the ditopic version of these chiral ligands.

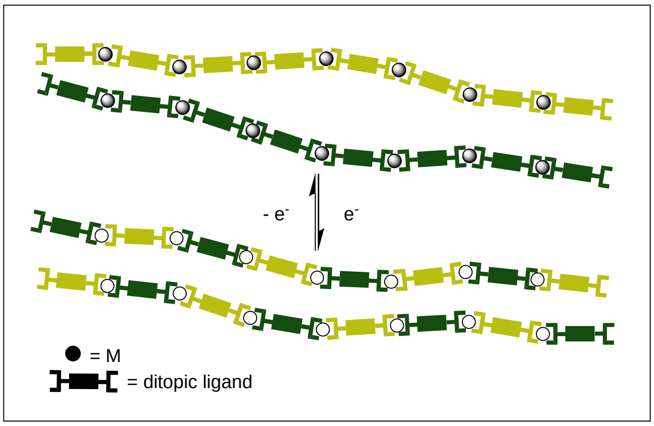


Figure 1 Principle of the electrochemically-induced control of the metallo-polymer arrangement: generation of block or alternating metallopolymers through the selective formation of homoleptic (top) or heteroleptic complexes (down).

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PHOTOLITHOGRAPHIE DE RÉSEAUX MAGNÉTO-OPTIQUE À PROPRIÉTÉS MODULABLES PAR PIÉZO-ÉLECTRICITÉ

Marwan Fakhry[1,2], O. Soppera[1,2], D. Berling[1,2]*

1. Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France
2. Université de Strasbourg, France
(Marwan.fakhry@uha.fr)

ABSTRACT:

The integration of magneto-optical (MO) components on conventional platforms (glass, polymer, SOI or semiconductor) is a technological challenge that has persisted since the first demonstration [1].
Indeed, MO materials need heat treatments at more than 700°C, incompatible with their integration within optical chips having other functions. It has also been demonstrated that the use of a 1D structuring acting as a distributed Bragg resonator enhances MO properties [2]. Our recent works show the possibility of realizing micro/nano structured MO networks by deep-UV photolithography at RT of a nanocomposite with high MO properties based on a sol-gel doped with magnetic nanoparticles (NPM) and their integrations for applications in guided optics and in free space [3].
Modulation and parameter tunability of MO gratings allow not only a means to adjust for manufacturing errors but also a mechanism to increase device functionality.
The goal is to study and control the modulation of photolithographed magneto-optical networks deposited on a thin layer of piezoelectric material (by applying a voltage). It is more suitable to use ferroelectric polymer materials such as poly (vinylidene fluoride) as they don't require HT treatment [4].
Ultimately, the objective is the complete realization at LT of modular non-reciprocal optical components, hybrid piezo-network MO structures, with a complete study of their properties (piezo, MO, ME coupling).
Currently, at the early stages of this work, we are focusing on the piezo-electric layer. The main goal is the optimization of its PE properties, mainly by maximizing the beta phase of the PVDF. Multiple formulations and coating methods had been used, and interesting results had been obtained using characterization techniques (FTIR, XRD, AFM, SEM, Profilometer…), while the topography and roughness, must also be controlled.
Many other challenges await us, like combining the 2 layers, accurately controlling the mechanical variation of the PE layer, and maximizing the faraday rotation of the MO layer.

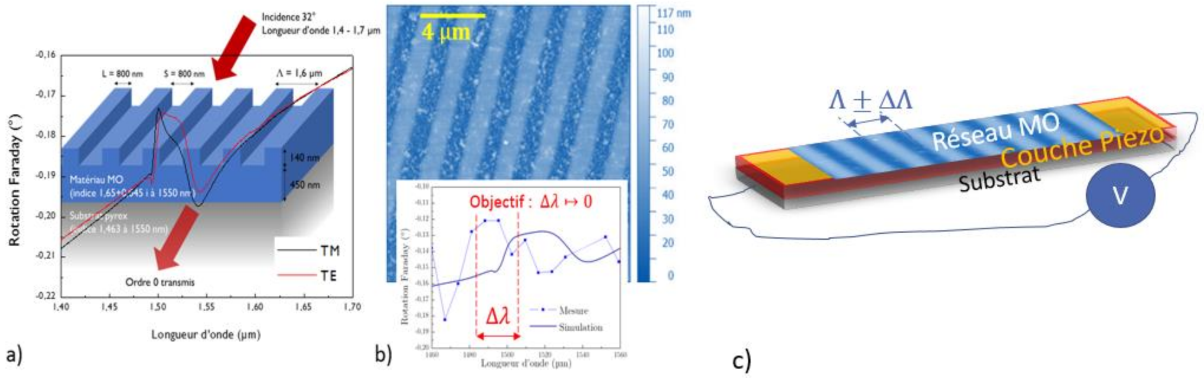

Figure 1: Simulation of a nanocomposite MO network (a), AFM image of a photolithographed network and measurement - simulation of its MO response (b), the device envisaged to modulate the MO properties using a piezoelectric layer (c).

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SYNTHESIS OF N-HETEROCYCLIC CARBENE-PLATINUM COMPLEXES TARGETING MITOCHONDRIA TO COMBAT GLIOBLASTOMA

Patricia Fernandez de Larrinoa[1,2], Antoine Kichler[2], Thierry Achard[1], Monique Dontenwill[3], Sylvie Fournel[2], Benoît Frisch [2], Jordan Parmentier[1], Béatrice Heurtault[2], Stéphane Bellemin-Laponnaz[1]

[1] DMO department, IPCMS, 23 Rue du Loess Bâtiment 69, 67200 Strasbourg;
[2] 3Bio Team, LCAMB, UMR 7199 CNRS/Université de Strasbourg, Faculté de Pharmacie, 74 route du Rhin, 67401 Illkirch Cedex;
[3] UMR 7021 CNRS, Faculté de Pharmacie, 74 route de Rhin, 67401 Illkirch Cedex;
(Béatrice Heurtault: bheurtault@unistra.fr and Stéphane Bellemin-Laponnaz: stephane.bellemin@ipcms.unistra.fr)

ABSTRACT:

Nowadays, glioblastoma is the most aggressive and most common brain tumor. Current therapy consists of a surgical resection followed by a combination of radiation and chemotherapy with temozolomide. However, the median survival rate for patients with treatment is approximately of 15 months, and these treatments are associated with numerous side effects [1]. It is now admitted that Cancerous Stem Cells (CSCs) are of particular interest because they play a key role in the therapeutic resistance of various cancers [2,3], like this one, which results in relapse, and therefore need to be eradicated.

The aim of this project is to design and evaluate new platinum complexes to simultaneously eradicate glioblastoma cancer cells as well as glioblastoma Cancerous Stem Cells. Considering that CSCs can be efficiently killed by compounds that alter the function of mitochondria [2], we propose the synthesis of N-Heterocyclic Carbene-platinum complexes presenting or not mitochondria targeting moieties, such as a triphenylphosphonium group.

So far, different platinum complexes have been synthetized and they were tested *in vitro* to determine their cytotoxicity on a human glioblastoma cell line (U87) as well as on a human glioblastoma stem cell line (NCH421K). The results show that several compounds possess a high capacity to kill both cancerous cell lines.

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Entry of Microparticles into Giant Lipid Vesicles by Optical Tweezers

<u>Florent Fessler</u>[1], Dr. Antonio Stocco[1]

[1] Institut Charles Sadron (ICS), Physics of Membranes and Soft Matter, Strasbourg, France;

ABSTRACT:

Interactions between micro- or nano-sized objects and lipid membranes are crucial in many processes such as entry of viruses in host cells, drug delivery or biomedical imaging. These processes rely on biological, chemical and physical interventions therefore involving specific as well as non-specific interactions. Indeed, the engulfment of a particle by a Giant Unilamellar Vesicle (GUV) membrane can be driven only by the adhesion strength due to non-specific interactions. Mechanical and thermomechanical properties of the membrane such as membrane bending resistivity and tension tend to work against the particle adhesion. Although an important amount of theoretical and computational physical models described the interaction of a particle with model membranes, experimental evidences reporting the existence of critical parameters responsible for the different dynamics observed upon contact and subsequent penetration are still lacking[1,2] In this work, we use optical tweezers to spatially trap a colloid, bring it in contact with a GUV and perform quantitative force measurements in the picoNewton range during particle entry into a GUV. By bright field and fluorescence microscopy, we are able to image the deformations of the membrane during the process. This allows to identify the conditions which need to be fulfilled in order to observe the entry of the particle and probe the reversibility of the process.

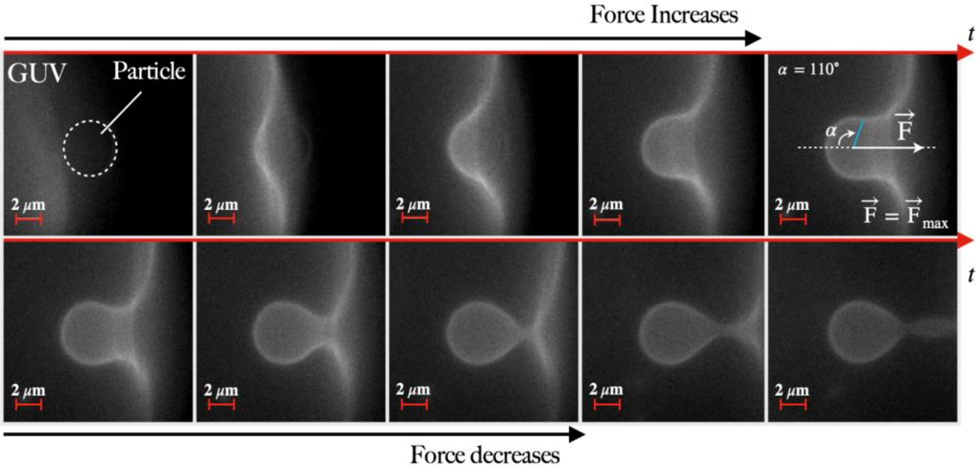

Figure 1: *Fluorescence microscopy snapshots of an optically trapped $R_p = 2.13\mu m$ silica particle forced to penetrate inside a GUV containing fluorescently labelled POPC lipids. The particle is not fluorescent and therefore not visible on these snapshots but its position can be inferred from the clear deformation of the membrane upon contact*.

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Development of multimodal platforms for photodynamic therapy

Figliola, C. [1] **and Ulrich, G.**[1]

[1] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (UMR 7515)
25 rue Becquerel, 67087 Strasbourg Cedex 2, France
(figliola@unistra.fr)

ABSTRACT:

Photodynamic therapy (PDT) is a medical treatment using the light in combination with a photosensitizer (PS) and molecular oxygen ($^3O_2$) against cancers and microbial infections.[1,2] The therapeutic effects of PDT derive from the absorption of the light by the PS, which reacts with $^3O_2$ and produces singlet oxygen ($^1O_2$) and other reactive oxygen species (ROS) causing cell death, vessel damage and an inflammatory and immune response.[1,2] Nowadays, although its minimal systematic invasiveness and toxicity, PDT is used as complementary to other established therapeutic solutions, such as radiotherapy, chemotherapy or surgery.[3] Our laboratory proposes the optimization of PDT-based therapeutic protocols by developing multimodal platforms including a two−photon absorption PS for PDT,[4] a one-photon absorption near-infrared (NIR) fluorophore for imaging and a targeting molecule, which has a high affinity for a specific biomarker of the chosen pathological condition. The selectivity of systems will be also obtained by the ability of PS to generate $^1O_2$ only into the targeted cells via stimuli-responsive reactions.[7] These systems will be accomplished in three parts. First, new difluoroboron pyridine-based complexes[5] and pyrrolyldipyrrins[6] scaffolds will be studied as potential PS. Secondly, the synthesis of theranostic dyads will be shown using the previously developed PS and NIR BODIPY-inspired fluorophores. Unlike the photosensitizing moiety, the fluorophores will be always active allowing the real-time visualization of the system towards its biodistribution, accumulation into the targeted tissues, body clearance, the PS-light administration interval and the light dose.[8] Last, investigation of potential organic platforms and optimization of the synthetic strategies to link covalently the PS, the NIR fluorophore and the targeting molecule will be presented.

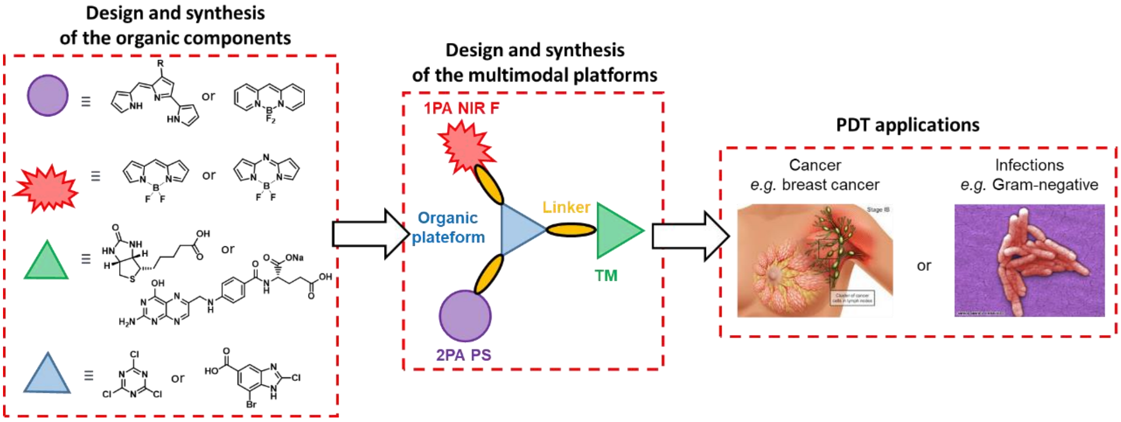

Figure 1 : Current research: development of multimodal organic platforms connecting a stimuli-responsive 2PA PS, a NIR imaging agent and a disease-targeting molecule.

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VERSATILE ACCESS TO TETRASUBSTITUTED 2-AMIDOACROLEINS THROUGH FORMAL SILYLFORMYLATION OF YNAMIDES

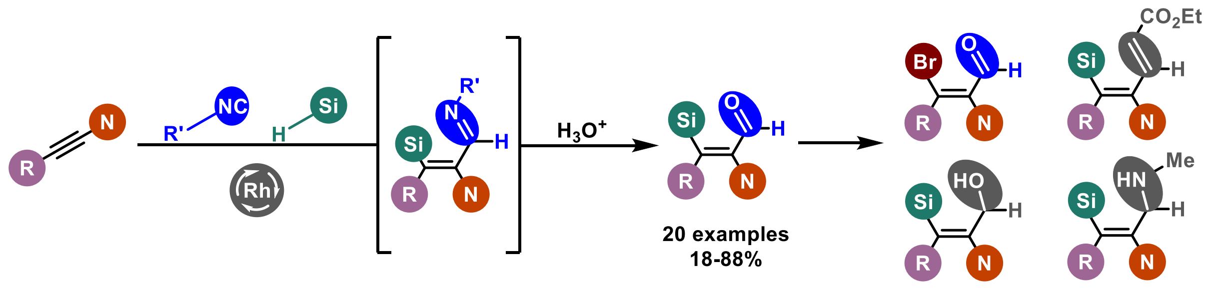
Stéphane Golling[1], Frédéric R. Leroux[1], Morgan Donnard*[1]

[1]*Université de Strasbourg, CNRS, Université de Haute-Alsace (LIMA UMR 7042), École Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087, Strasbourg, France*

ABSTRACT:

While the silylformylation reaction of terminal alkynes is now well studied, very few examples of internal alkynes are reported, mainly due to the stereo- and regioselectivity issues. To overcome this problem, we have turned our attention to the use of ynamides as the alkyne substrate in this transformation. Indeed, the silylformylation of ynamides could lead to the formation of tetra-substituted amidoacroleins that could be easily converted into different functionalities. Furthermore, the silylformylation reaction requires specific equipments (high pressure reactor, CO detector) and, as a better alternative, methodologies based on CO-surrogates are highly desirable.

In this context, inspired by Fukumoto and Chatani,[1] we developed a rhodium-catalyzed silylformylation involving an ynamide, a silane and an isocyanide. After a quick optimization, we demonstrated the almost complete stereoselectivity of our reaction for the syn-addition. Moreover, this reaction appeared to be completely regioselective towards the formation of the 2-amidoacrolein adduct. This reaction also tolerated different functional groups on the ynamide, the silane and the isocyanide starting material leading to a high degree of diversity on the final compound. In addition, these 2-amidoacroleins could be converted into a large variety of compounds thus demonstrating the potential of this building block.[2]



20 examples
18-88%

- Tetra-substituted amidoacroleins
- Versatile building blocks
- CO Free silylformylation
- High regio- and stereoselectivity

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Development of nanoporous membranes dedicated to insulin delivery for the treatment of diabetes using an eco-efficient approach

Bryan Gross[1], Guy Schlatter[1], Emeline Lobry[1], Anne Hébraud[1],

[1] ICPEES, Polymer Engineering Department, Institut de Chimie et Procédés pour l'Energie,
l'Environnement et la Santé, ICPEES UMR7515, Université de Strasbourg; 25 rue Becquerel,
Strasbourg Cedex 2 67087, France.
E-mail: bryan.gross@unistra.fr

ABSTRACT:

16 lines or 300 words

The DECAPES project aims at developing a semi-permeable membrane by electrospinning, a process allowing the fabrication of nanofibrous membranes from polymer solution subjected to a high electric field. This membrane is subsequently integrated into a cellular encapsulation device resulting to a "bioartificial" pancreas intended to restore normal insulin production for type 1 diabetic patients. The membrane must allow nutrients, glucose, and oxygen to enter into the bioartificial pancreas to provide the necessary environment for the survival and activity of the encapsulated cells which in turn produce insulin. These secreted molecules can then exit the device through the pores of the membrane. On the other hand, the molecules of the immune system cannot enter the device, preventing the rejection of the cells contained in the medical device (figure 1).

In this context, the PhD project is based on the development of a polymer membrane with controlled pore size by "green electrospinning", using only water as solvent [1]. One of the major challenges is to reduce the pore size of the membrane to less than 100 nm preferentially. To achieve this, an innovative strategy is the development of a composite membrane by involving a thermoplastic polymer and a water-soluble polymer as a sacrificial element, whose melting temperature is lower than that of the thermoplastic polymer. After a thermal compression, the water-soluble fibers will generate a continuous nanoporous pathway along the thermoplastic molten membrane. A water wash will finally remove the water-soluble fibers and keep the nanoporous traces of the polymer membrane in a controlled way.

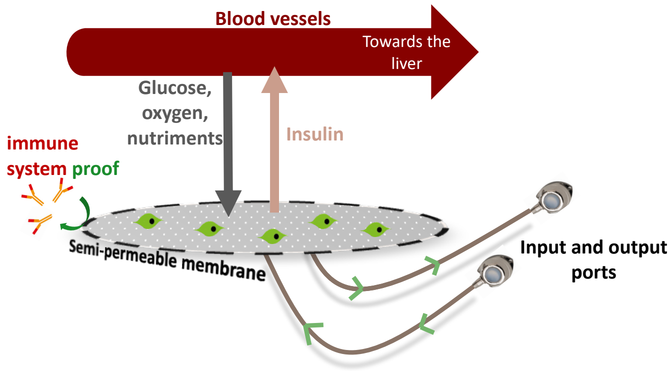

Figure 1 Explanatory scheme of a cell macro-encapsulation device

Reference

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Au/ (B OR C) DOPED g-C_3N_4/ TiO_2 NANOCOMPOSITES FOR PHOTOREDUCTION OF CO_2 WITH WATER IN THE GAZ PHASE INTO CH_4

Leila Hammoud[1,2], Valérie Caps[1], Joumana Toufaily[2], Taysir Hamieh[2], Valérie Keller[1]
[1] ICPEES, UMR 7515 CNRS, 25 rue Becquerel 67087 Strasbourg cedex, France.
[2] MCEMA, Lebanese University, Beyrouth, Liban.
leila.hammoud@etu.unistra.fr.

ABSTRACT:

Photocatalytic CO_2 reduction with water in the gas phase (artificial photosynthesis) into methane is one of the most useful routes to recycle CO_2. Among of the possible semiconductor (SC) photocatalysts, g-C_3N_4 and TiO_2 are interesting due to their abundance, low cost, chemical and thermal stability, and non-toxicity. The limited solar absorption and high recombination rate of photogenerated charge carriers of these materials however severely impede their applications. Several strategies have been considered to overcome these limitations such as SC doping, heterojunction formation and co-catalyst addition. We have recently shown that an efficient heterojunction between C_3N_4 and TiO_2 could be engineered by polycondensing C_3N_4 precursors impregnated on pre-formed TiO_2 nanocrystallites acting as hard templates [1]. This method yields few layer C_3N_4 films in strong interaction with TiO_2, which give highly efficient Au/C_3N_4-TiO_2 photocatalysts for water splitting [1]. However, these composites did not allow us to get CH_4 in the photoreduction of CO_2 with H_2O in the gas phase using visible illumination.

Here we show that an efficient heterojunction with enhanced absorption properties can be constructed for CO_2 photoreduction with H_2O under visible light by a modified polycondensation method, using urea as C_3N_4 precursor together with boric or citric acid [2,3] which will dope the C_3N_4 structure. The nanocomposites Au/B-g-C_3N_4/TiO_2 and Au/C-g-C_3N_4/TiO_2 showed average CH_4 production rates (fig.1) during 10h (8 and 34 times higher, respectively, than those obtained on Au/TiO_2 or Au/g-C_3N_4/TiO_2).

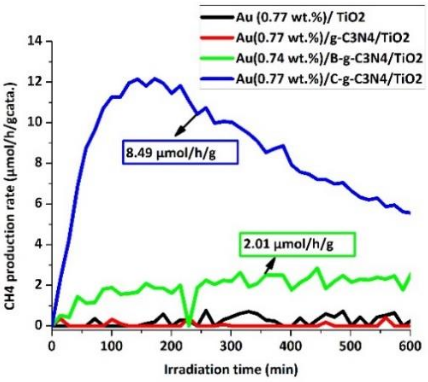

Figure 1: Average CH_4 production rate (during 10 h) for Au/TiO_2, Au/g-C_3N_4/TiO_2 and Au/(B or C) doped g-C_3N_4/TiO_2.

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Pd-Catalyzed Silylcyanation of Ynamides: Regio- and Stereoselective Access to Tetrasubstituted 3-Silyl-2-Aminoacrylonitriles

Pierre Hansjacob[1], Frédéric Leroux[1], Vincent Gandon*[2,3], Morgan Donnard*[1]

[1]Université de Strasbourg, UHA, CNRS, UMR 7042, LIMA, ECPM, Strasbourg, France;
[2]Université Paris-Saclay, CNRS, UMR 8182, ICMMO, Orsay, France;
[3]Ecole Polytechnique, Institut Polytechnique de Paris, CNRS, UMR 9168, LCM, Palaiseau, France
(vincent.gandon@universite-paris-saclay.fr ; donnard@unistra.fr)

Enamines as well as acrylonitriles are valuable building blocks in organic chemistry. However, the synthesis of scaffolds merging both functionalities namely aminoacrylonitriles are particularly difficult[1]. In 1985, Chatani and co-workers published a palladium-catalyzed addition of trimethylsilyl cyanide on terminal alkynes to provide cyano-substitued vinylsilanes in good to high yields with high regio- and stereoselectivity[2]. In this communication we will introduce how we took advantage of specific polarized alkynes (i.e. ynamides) to produce efficiently polyfunctionalized tetrasubstituted olefins, so-called 2-aminoacrylonitrile derivatives, in a stereo and regio-selective manner. DFT investigations allowed us to explain the divergence of stereoselectivity observed experimentally according to the substitution of the alkyne. These unique building blocks are particularly interesting as they can undergo a broad range of post-functionalization reactions such as vinylsilane, nitrile and enamine chemistry[3].

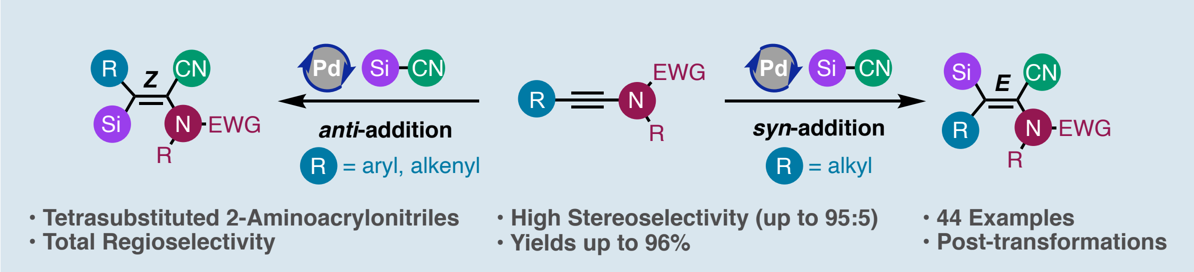

Figure 1: Pd-Catalyzed Silylcyanation of ynamides

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EQUILIBRIUM SHAPES OF THIN ELASTIC RIBBONS IN SIMPLIFIED FOAMS

Manon Jouanlanne[1], Antoine Egelé[1], Damien Favier[1], Wiebke Drenkhan[1], Jean Farago[1], Aurélie Hourlier-Fargette[1]

[1] Institut Charles Sadron, Unistra & CNRS UPR 22, Strasbourg
(corresponding author: hourlierfargette@unistra.fr)

ABSTRACT:

Combining soft materials with fluids leads to rich systems in which elasticity and capillarity come into play, in particular in the case of slender elastic structures. Strategies using elastocapillarity to control the architecture of mechanical assemblies have recently highlighted ways to fold, spool or assemble elastic objects [1]. However, those intelligent design approaches remain unexplored in the context of liquids with a hierarchical architecture, such as foams.

In the context of the FoamFibMat project supported by ITI HiFunMat via a Starting grant, we investigated the competition between elasticity and capillarity in a 2D foam column upon introduction of an elastomer ribbon (Fig.1). In the low-density limit, bubble arrangements and foam structures are governed by Plateau's laws, corresponding to the minimisation of interfacial energies [2]. Confining bubbles into tubes leads to periodically ordered structures which are controlled by the ratio of tube width to bubble diameter: as a model system, we consider the so-called staircase structure formed in a square section tube where bubbles of equal volume are rearranged in a staggered pattern [3]. This quasi-2D structure has central soap films connected at 120 degrees angles, in which we introduce elastic ribbons of different bending rigidities. Using X-ray micro-tomography, we quantify the equilibrium shapes of the foam/ribbon systems. We provide a detailed analysis of the ribbon profile, that compares well with theoretical predictions in the whole range of bending rigidities. In addition, our proof-of-concept experiments show that such setup can be used as a method to mold materials with characteristic shapes and curves imprinted by the foam structure. This can be imagined as a first step towards the design of composite materials with new architectures based on solidification of the whole system.

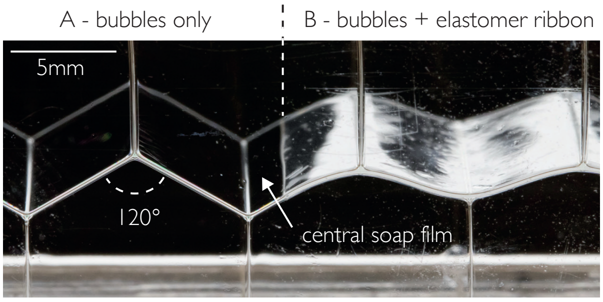

Figure 1: Staircase structure of bubbles in a container with square cross-section without (A) and with (B) an elastomer ribbon inserted inside the central soap film.

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Preparation and characterization of a novel organo-montmorillonite as superb adsorbent for toxic organic dye

Redouane HAOUNATI[1] Hamza Ighnih[1], Hassan OUACHTAK[2], Siham AKHOUAIRI[1], Fadwa LARGO[1], Naima Hafid[3], Amane JADA[4], Abdelaziz AIT ADDI[1]

[1]Physical Chemistry and Environment Team (ECPE), Ibn Zohr University, Agadir, Morocco.

[2]Laboratoire de Chimie Appliquée & Environnement, Equipe Bio organique Appliquée, Faculté des sciences, Université Ibn Zohr, Agadir, Morocco.

[3]Centre Régional des Métiers de l'Education et de la Formation, Souss Massa, Morocco.

[4]Institute of Materials Science of Mulhouse (IS2M, CNRS-UHA), Mulhouse, France (amane.jada@uha.fr)

ABSTRACT:

We carried out batch adsorption experiments, of malachite green from water onto organo-montmorillonite SDS/CTAB@Mt. Both adsorption isotherms and kinetics were determined. In addition, parameters affecting the adsorption process, such as the adsorption temperature, the aqueous phase pH, the adsorbent amount. The optimum conditions were obtained at pH 7, 0.1g of adsorbent dosage, and 60 min of agitation time. Such optimum conditions were thereafter utilized in the kinetic and isotherm adsorption studies. Two kinetic models were applied to analyse the kinetic data, and pseudo-second order was found to be the best fitted model with $R^2 > 0.999$. At the equilibrium, the obtained adsorption isotherms were found to be well described by Langmuir isotherm model suggesting that the dye were adsorbed homogenously over a monolayer surface of organo-montmorillonite SDS/CTAB@Mt. To elucidate the adsorption mechanism, the thermodynamic parameters, such as ΔH°, ΔS° and ΔG°, were also assessed and their values revealed that the adsorption reaction was spontaneous, exothermic and resulted in a decrease of the MG adsorbed molecules randomness on the adsorbent surface.

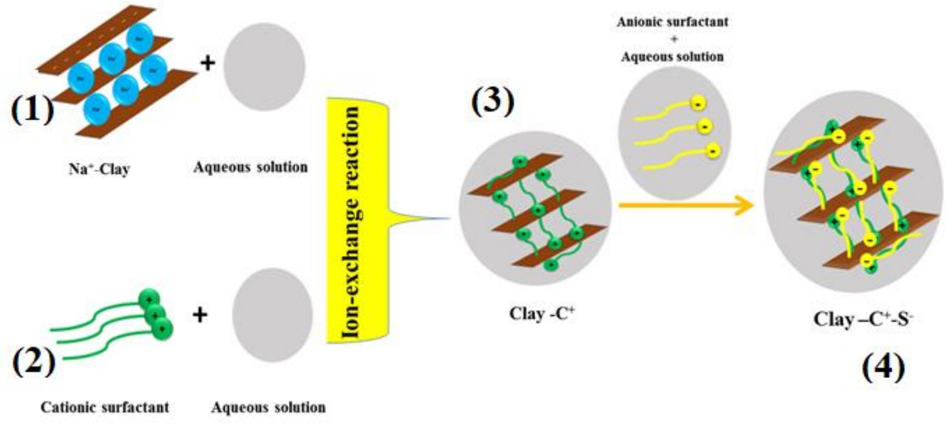

Figure 1: Sample preparation. (1) The MNT dispersed in deionized water. (2) The surfactant (CTAB) dispersed in deionized water. (3) The ion exchange reaction between Na and CTAB allows to obtain a MNT@CTAB composite. (4) The electrostatic interaction between CTAB and SDS provides MNT@CTAB-SDS a new composite.

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Design of Catalytic Adsorbents for Wastewater Treatment

Abdellah AIT EL FAKIR[1,2], Amane JADA[2], Zakaria ANFAR[1,2,3] and Noureddine EL ALEM[1]

[1]Laboratory of Materials & Environment (LME), Ibn Zohr University, Agadir, Morocco

[2]Institute of Materials Science of Mulhouse (IS2M), Haute Alsace University, Mulhouse, France

[3]Institute of Chemistry & Biology of Membranes & Nano-objects (UMR5248 CBMN), CNRS, Bordeaux University, Institut Polytechnique Bordeaux 2 rue Robert Escarpit, Pessac, France.
(amane.jada@uha.fr)

ABSTRACT:

Water pollution results from anthropogenic activities which generate the release in the aquatic medium of urban, agricultural or industrial pollutants having harmful ecological effects. For the remediation of these pollutants, various methods including filtration, coagulation/flocculation, reverse osmosis, chemical oxidation, photocatalytic processes, adsorption-complexation. The adsorption process, in comparison to the others methods, is commonly used in water and wastewater treatment methods, due its simplicity of design, easy operation, high efficiency, and availability of the adsorbent. Thus, in the last three decades much research have been devoted to design efficient adsorbents and catalysts for wastewater treatment and to preserve environment. In the present work, we give a general overview on the design of the adsorbents and catalysts, used in the wastewater treatment by using the adsorption process. It outlines mainly the use of carbonaceous adsorbents for organic pollutant removal. Additionally, this work discusses the advanced oxidation processes (AOP), producing highly reactive species from various peroxides, which allow total destruction of organic pollutants present in the wastewater.

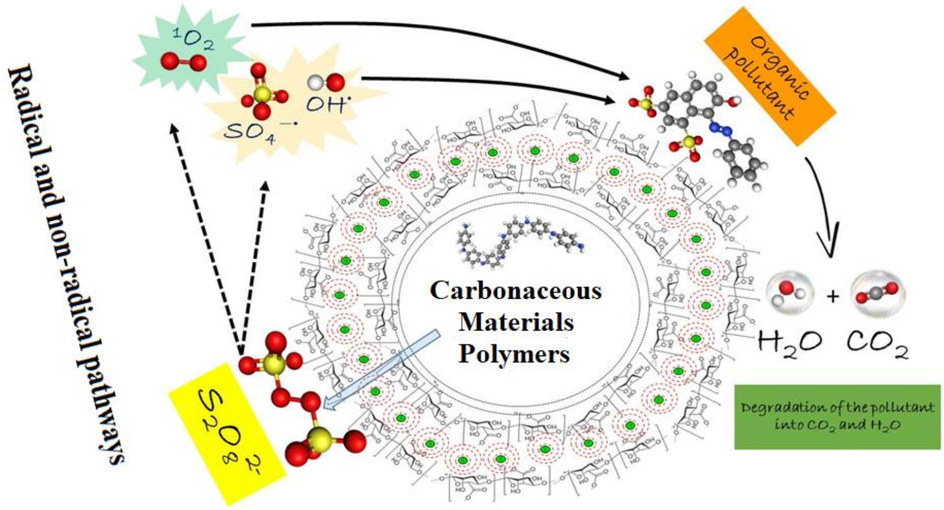

Figure 1: Alginate pearl coating carbonaceous materials [1, 2]

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Spectroscopic study of plasmon-induced photopolymerization

Amine Khitous,[1,2]_OlivierSoppera[1,2,*]

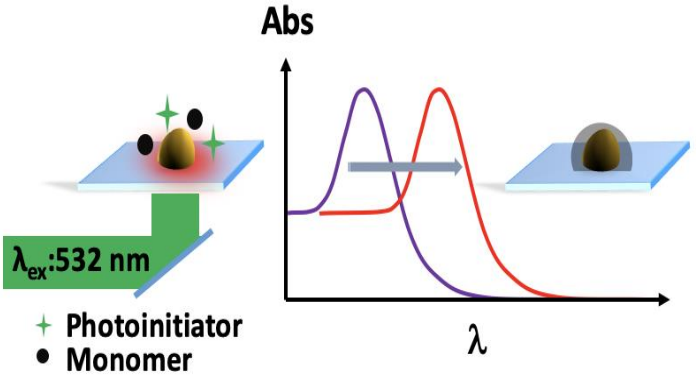
[1] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France;
[2] Université de Strasbourg, F-67081Strasbourg,France

(amine.khitous@uha.fr)

ABSTRACT:

The dielectric function of metallic nanoparticles depends mainly on their surrounding environment. A small variation of the medium refractive index due to chemical or physical interaction induces a shift in the plasmonic band of the NPs (LSPR). In this context, we used gold nanoparticles (AuNPs) prepared by thermal dewetting of an Au thin film as nanoprobes to follow the photopolymerization at the surface of AuNPs by means of a fiber UV-vis spectrometer. To show the interest of this approach, two configurations were used: resonant and non-resonant excitation between the photopolymer and the AuNPs were investigated. We have shown that these AuNPs not only allowed the monitoring of the induced photopolymerization at the nanoscale, but also to highlight the near field coupling effect responsible for the acceleration of the photoinduced reactions.

This methodology seems very interesting to study the photoinduced nanofabrication processes of metal/polymer hybrid nanoparticles, and more globally to study the photopolymerization reactions at the nanoscale.



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Direct Deep UV (DUV) photopatterning of metal oxide thin films from nanocrystal (NCs) colloids: a simpler and faster process at room temperature

Quentin KIRSCHER,[1] **Dominique BERLING**,[1] **Fabien GRASSET**,[2] **Olivier SOPPERA** [1]

[1] *Institut de Science des Matériaux de Mulhouse (IS2M), UMR7361 CNRS-UHA, Univ. de Haute-Alsace, 15 rue Jean Starcky 68057 MULHOUSE*
[2] *Institut des Sciences Chimiques de Rennes (ISCR), UMR6226 CNRS-UR1, Univ. de Rennes 1, 263 avenue du Général Leclerc 35042 RENNES*
Emails: olivier.soppera@uha.fr, dominique.berling@uha.fr

Deep UV photolithography (193 nm) is a reference technique for micro/nanopatterning. The photoresists used, which are exclusively organic, have only a sacrificial role and do not contribute to the final properties of the material. This also adds a significant number of steps and the use of corrosive products in the process. In the case of metal oxides, several studies have already made it possible to considerably reduce the number of steps by directly structuring the material using hybrid photoresists [1, 2]. The produced oxide is however amorphous and a high-temperature annealing step is necessary to obtain the crystalline phase, ruling out the application to flexible substrates. A possible solution is to start directly from the oxide in the form of NCs and to assemble them. This approach has already been successfully tested in the case of quantum dots (CdS, CdSe) and for micrometric resolutions [3] but always involving toxic products. The objective is to propose an original direct nanopatterning approach using colloidal NCs as "building blocks" that assemble under the effect of DUV light, while being more environmentally friendly (abundance, toxicity).

Using FTIR and XPS spectrocopies, ellispsometry and XRD characterizations, it has been observed that the assembly of NCs results from a spatially controlled aggregation following the degradation of ligands on the surface without modification in size of the NCs (**Fig. 1**). The study focuses mainly on ZnO but the wide variety of oxides that can be synthesised in the form of NCs encourages a generalisation of the process to other oxides.

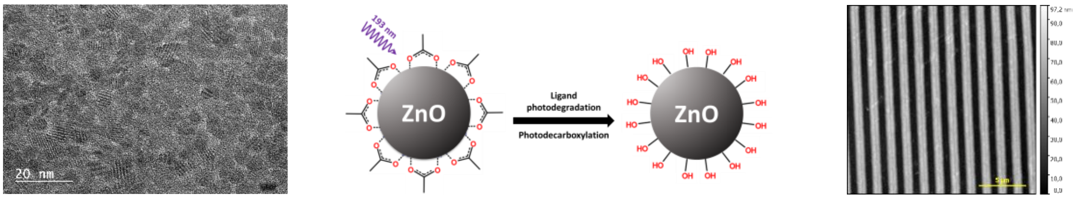

Figure 1 : **From colloids to microstructures by ligand photodegradation under DUV exposure.**

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Salt-assisted compaction for the design of porous albumin scaffolds for the delivery of antitumor drugs

Guillaume Leks[1], Eya Aloui[1], Jordan Beurton[1], Claire Medemblik[2,3], Benoît Frisch[1], Philippe Lavalle[2,3]

[1] Laboratoire de Conception et Application de Molécules Bioactives, CNRS UMR 7199, Université de Strasbourg, Faculté de Pharmacie, Illkirch, France

[2] Laboratoire de Biomatériaux et Bioingénierie, INSERM UMR 1121, Université de Strasbourg, Strasbourg, France

[3] Faculté de Chirurgie Dentaire, Université de Strasbourg, Strasbourg, France

Keywords: albumin, porous material, antitumor, drug delivery

ABSTRACT

After surgical extraction of solid tumors, the treatment of residual cancer cells is essential to prevent recurrence. Furthermore, the filling of the gap left by the tumor mass requires the use of appropriate biodegradable materials. To tackle these issues, we design a porous material entirely made of albumin for the delivery of doxorubicin, a potent anti-tumor drug. This material is prepared using salt-assisted compaction, which is a patented (European patent application EP3811982) procedure for the preparation of albumin materials in non-denaturing conditions and without the use of toxic crosslinking agents. Solutions of human serum albumin (HSA) and salt (NaBr) are prepared in a sodium acetate buffer (0.2 M, pH 6) and emulsified through intense stirring to obtain homogenous foams. Then, these foams are evaporated at 37°C until the formation of solid materials. After elimination of the salt by washing in water, the obtained materials are entirely made of water-insoluble albumin. These materials are highly porous with interconnected pores. After investigating the effect of the formulation parameters on the formation of these materials and their porosity (pH, salt concentration, and stirring procedure), we show that the pore size of these materials is tunable in a range of 200 to 600 µm according to the tested formulations. After additional characterization, these porous materials are successfully loaded with doxorubicin using a post-loading approach.

Photovoltaic spatial light modulators for self-powered smart windows

Yuhan Zhong[1,2], Jing Wang[1], Sadiara Fall[1], Yaochen Lin[1], Nicolas Brouckaert[3], Chaima Mahmoudi[4], Wenziz Muzuzu[4], Nicolas Leclerc[4], Malgosia Kaczmarek[3], Martin Brinkmann[2] and Thomas Heiser[1*]

[1] Laboratoire des sciences de l'Ingénieur, de l'Informatique et de l'Imagerie (ICube), Université de Strasbourg, CNRS, 23, rue du Loess 67037 Strasbourg, Cedex 2 France;
[2] Institut Charles Sadron, CNRS - UPR 22, 23 rue du Loess, Strasbourg 67034, Cedex 2 France
[3] University of Southampton, Southampton, United Kingdom
[4] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, Université de Strasbourg, CNRS, 25, rue Becquerel 67085 Strasbourg Cedex, France
(Thomas HEISER: thomas.heiser@unistra.fr)

ABSTRACT:

Photovoltaic spatial light modulators form a new class of dynamic glazing that could be of interest to smart windows applications. The structure of the modulators includes a twisted nematic liquid crystal layer and an organic donor-acceptor bulk heterojunction. The latter is in contact with the liquid crystal and is used as a molecular alignment layer. In addition, under illumination, the bulk heterojunction generates an electric field that can be strong enough to orient the liquid crystal molecules homotropically and change the device optical transmittance, without requiring an external power source. The transmittance of this hybrid device adjusts spontaneously to ambient light within less than a second, with a sensitivity that can be tuned by a passive resistor. While this unique combination of features is desirable for smart windows, the device maximum transmittance in the clear state is currently limiting the possible scope of application.

In this contribution, we will firstly present the detailed structure, elaboration procedure and optical properties of a first generation of photovoltaic spatial light modulators that are based on commercially available polymer:fullerene blends and liquid crystals. The physical mechanism underlying the device operation will be demonstrated by crossed-polarizer intensity measurements as a function of incident light intensity and applied voltages. Furthermore, the time-dependent transmittance of a device that is exposed to a pulsed light source will be presented in order to assess its response time and reversibility.

In the second part we will describe various routes that we are following to improve the device optical properties in terms of maximum transmittance and sensitivity to ambient light. In particular, a new high band-gap semiconducting molecule that has been designed to achieve a highly transparent bulk heterojunction layer and increase the photo-induced electric field will be presented and its utilization in photovoltaic spatial light modulators will be shown.

TITLE: DEVELOPMENT OF VIRUS-LIKE PARTICLE PLATFORM FOR THE CONTROL OF CELL BEHAVIOR

Hasna Maayouf [1], Thomas Dos-Santos [2], Isabelle Brigaud [3], Tatiana Petithory [4], Karine Anselme [5], Carole Arnold [6] and Laurent Pieuchot [7]

Université de Haute-Alsace, IS2M-CNRS 7361, F-68100 Mulhouse, France
hasna.maayouf@uha.fr[1], *thomas.dos-santos@uha.fr*[2] , *isabelle.brigaud@uha.fr*[3],
tatiana.petithory@uha.fr[4], *karine.anselme@uha.fr*[5], *carole.arnold@uha.fr*[6], *Laurent.pieuchot@uha.fr*[7]

ABSTRACT:

Virus-Like Particles (VLPs) are self-assembled protein-based nanoparticles that provide versatile delivery platforms for a variety of biomedical applications thanks to their biocompatibility and their ability to encapsulate therapeutic molecules[1,2]. However, the field of biomaterials still makes little use of these tools. Here we show that VLPs can be used to develop cell-signaling nanoscaffolds that can control cell behavior. Using cloning techniques, we fused short bioactive peptides to the C-terminus of the CP3 coat protein. We produced recombinant particles expressing adhesion (RGD) and osteogenic (BMP2) peptides at their surface and purified them by affinity and size exclusion chromatography techniques. We show that VLP-RGD particles stimulate adhesion and cell spreading with the same efficacy as native fibronectin whereas VLP-BMP2 particles do not. With similar methods, we were able to produce heteromeric particles co-expressing RGD and BMP2 peptides. We showed that the presence of RGD and BMP2 peptides on our multifunctional particles can promote cell adhesion similarly to VLP-RGD. These results show that our particles can be used as a platform to control cell adhesion for biomaterials applications.

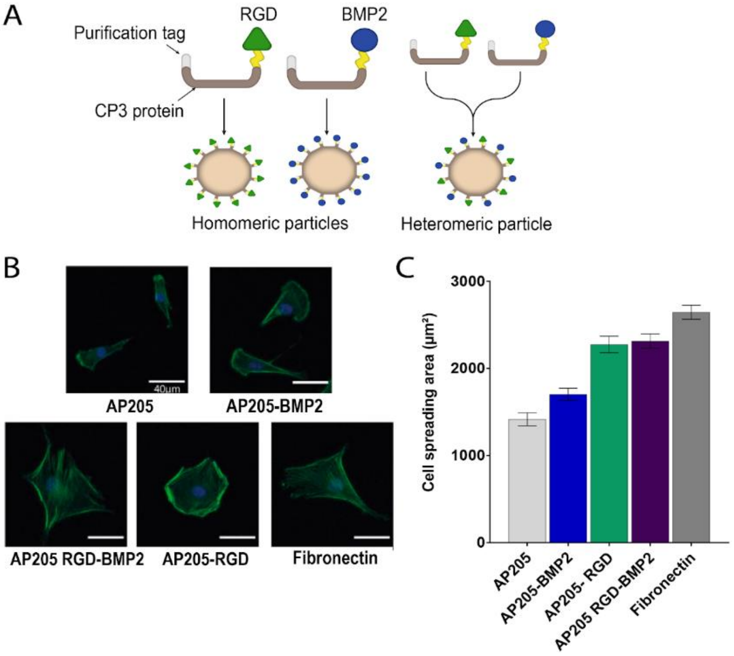

Figure 1: A Virus-Like Particle platform for the control of cell behavior. Schematic representation of AP205 VLPs constructions made (A). Immunostaining of C2C12 cells after 6h of incubation on PDMS surfaces treated with AP205 particles and fibronectin at concentrations of 200 µg/mL. Scale bar: 40 µm (B). Quantification of cell spreading area in µm² measured on each condition (C).

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EXPLORING HYDROGEN-BONDIND AND SUPRAMOLECULAR CHIRALITY IN ORGANIC ELECTRONICS

Amparo Ruiz-Carretero[1], Ana M. Garcia [1], Gabriel Martinez [1], Ricardo Avila-Rovelo[1], Joshua Humphreys[1], Shu Seki[2]

[1] Institute Charles Sadron, Team SYCOMMOR, Strasbourg, France;
[2] Kyoto University, Department of Chemical Engineering, Kyoto, Japan
(amparo.ruiz@ics-cnrs.unistra.fr)

ABSTRACT:

The presence of noncovalent interactions in organic semiconductors has been demonstrated to be beneficial in several applications, resulting in the enhancement of charge transport and device efficiency. Particularly, the incorporation of H-bonds in organic semiconductors has been proven to increase solar cell efficiency by 50%.[1] Nevertheless, the race for achieving efficiency records, has hampered research focused on solving other fundamental issues. Regarding hydrogen-bonding, no comparative studies have been performed, finding scattered examples in literature with different semiconductors, H-bonding units and without complete studies including both, the optoelectronic and self-assembly properties.[2] The main goal of our research is to understand the impact of hydrogen bonds in supramolecular electronics to apply them efficiently in devices. Here we show a comparative study using diketopyrrolopyrrole (DPP) as a model system[3] (Figure 1) and how the results are translated into state-of-the-art materials, such as quinquethiophene-rhodanine and isoindigo derivatives (Figure 1). Different families of hydrogen-bonded DPP supramolecular polymers displaying different hydrogen-bonding parameters will be discussed,[3] including the role of chirality[4]in the final electronic properties.

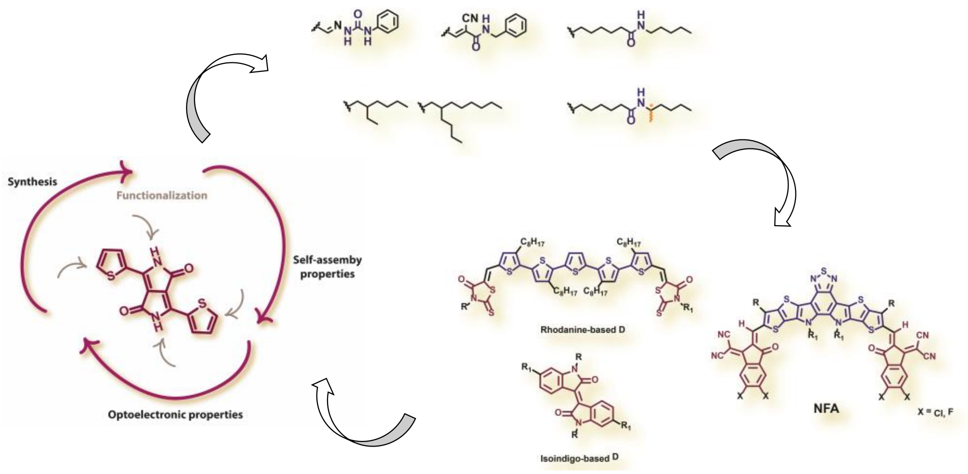

Figure 1 : Model system for the study of hydrogen-bonding in organic electronics, followed by the parameters to be explored and the expansion to state-of-the-art semiconductors

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Control of π-interactions in conjugated (macro)molecular systems for organic electronics

Stéphane Méry [1], **Benoît Heinrich** [1], **L. Mager** [1], **Jean-Charles Ribierre** [2],
Nicolas Leclerc [3], **Patrick Lévêque** [4], **Thomas Heiser** [4]

[1] IPCMS, CNRS-Université de Strasbourg;
[2] OPERA, Université de Kyushu, Fukuoka, Japon & SPEC, CEA-Saclay, Gif Sur Yvette
[3] ICPEES, CNRS-Université de Strasbourg
4 ICube, INSA-CNRS-Université de Strasbourg
Contact: stephane.mery@ipcms.unistra.fr

ABSTRACT:

Molecular organization is a parameter of primarily importance as it affects the properties of the materials. The control of the molecular organization of π-conjugated systems can be achieved through a reasoned functionalization by flexible chains (usually aliphatic chains). The natural molecular segregation between these chains and the conjugated moieties may lead to the formation of mesomorphic organizations whose structural features can be tailored using geometric molecular parameters, in particular.

In this communication will be described the original functionalization by short siloxane chains. Compared to aliphatics, siloxane chains present a greater flexibility and a greater segregating power which allows a finer control of the organizations and the intermolecular interactions. Through some selected examples, we will illustrate the impact of siloxane chain functionalization to stabilize a complex donor-acceptor molecular system into a smectic liquid crystal organization,[1,2] or else to stabilize conjugated polymers with enhanced π-stacking interactions, ultimately leading to enhanced charge transport properties (see figure).[3]

Through other examples, we will show how functionalization with siloxane chains led to the preparation of π-conjugated molecular liquids.[4,5], e.g. compounds that are in a stable liquid state (without solvent) at room temperature. The structural characterization by X-Ray scattering shows that short-range π-molecular interactions are preserved in the liquid state, allowing us to explain the significant electronic conduction measured in these liquid molecular systems.[4]

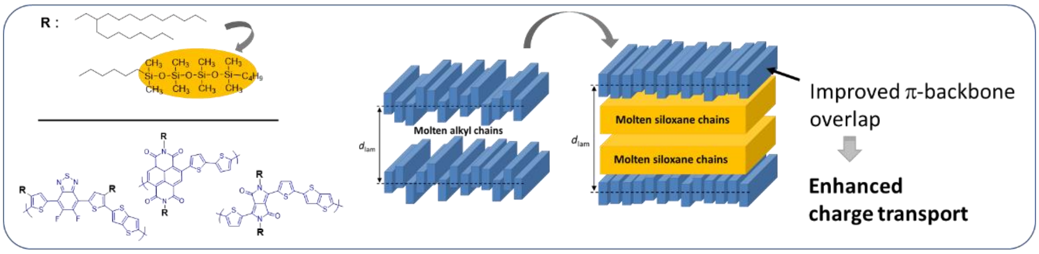

Figure. Illustration of the enhanced polymer π-stacking overlap by aliphatic-to siloxane substitution, ultimately leading to a significant improvement of charge transport properties

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TOWARDS THE SYNTHESIS OF ENANTIOENRICHED DIFLUOROMETHYL AND DIFLUOROMETHYLENE SCAFFOLDS

Amélia Messara[1], **Armen Panossian**[1], **Gilles Hanquet**[1*], **Frédéric R. Leroux**[1*]

[1] *Université de Strasbourg, Université de Haute-Alsace, CNRS, LIMA UMR 7042, ECPM, 25 rue Becquerel, 67087, Strasbourg, France*

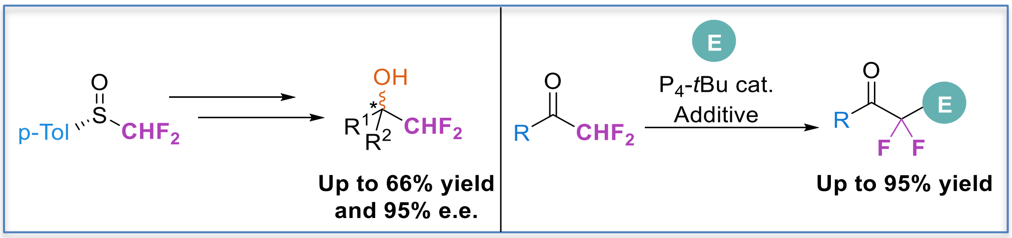
amelia.messara@etu.unistra.fr, Frederic.leroux@unistra.fr, ghanquet@unistra.fr

ABSTRACT:

Within fluorinated moieties, the –CHF$_2$ group has aroused a growing interest in pharmaceutical and agrochemical fields in the last few years. Several chemists have already reported the synthesis of difluoromethylated compounds but the enantioselective introduction of the difluoromethyl motif has been scarcely described yet. Additionally, the synthetic access to difluoromethylene scaffolds remains underdeveloped. In this context, we desired to develop new pathways to access enantiopure difluoromethyl or difluoromethylene scaffolds. We were also focused on the deprotonation of the –CHF$_2$ group, which remains very challenging due to the poor stability of the generated carbanion.

Therefore, we recently developed a new strategy to synthesize enantiopure difluoromethyl sulfoxides, that were further used as chiral auxiliaries to obtain enantioenriched difluoromethyl alcohols through deprotonation of the sulfoxide.[1] At the same time, the acidity of diverse difluoromethyl sulfoxides was investigated by UV-visible spectrophotometry.[2] In relation with the deprotonation of the corresponding sulfoxides, we also managed to perform the deprotonation of difluoromethyl ketones with a catalytic organosuperbase followed by trapping with various electrophiles to access highly valuable difluoromethylene compounds.

Figure 1 : Deprotonative functionalization of difluoromethyl ketones



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Development and characterization of nano-fibrous membrane for the treatment of congenital diaphragmatic hernia

Rodolphe Migneret[1], Anne Hébraud [1], Guy Schlatter[1], Emeline Lobry[1], Nadia Bahlouli[2], Hamdi Jmal[2], Cendrine Seguin[3], Benoit Frisch[3], Julie Favre[3], Vincent Ball[4], Isabelle Talon[4]

[1] ICPEES, UMR 7515, Strasbourg France;
[2] ICube, UMR 7357, Strasbourg France;
[3] CAMB, UMR 7199, Strasbourg France;
[4] Inserm, U1121, Strasbourg France;
(corresponding author: rodolphe.migneret2@etu.unistra.fr)

Abstract

Congenital Diaphragmatic Hernia is a rare malformation, a hole in the diaphragm is formed early in the embryogenesis. The consequences are multiple. At the birth of the child, a surgery is required and in half of the cases, a prosthesis is necessary to fill the hole. The currently used prosthesis are not intended for this application, it is not enough stretchable due to its high stiffness, and therefore, often lead to the breaking of stiches and a recurrence of the hernia. The aim of my PhD is to design a new prosthesis for this specific application that will be easily and highly stretchable to follow the growth of the child. Using electrospinning, a membrane is formed, having a fibrous surface that mimic the extra-cellular matrix and thus enhance cell colonization for a better integration to the diaphragm. For the moment, the first results highlight a good biocompatibility and more than 300% stretchability (enough for the growth of the child). One of the issue of the membrane elaboration concerns its thickness, which has to be as homogenous as possible to avoid any differences in the mechanical properties. To solve this problem, we have studied the thickness profile of the fibrous mat on the collector as a function of the emitter used (multiple needles or needle-free) and its translation with respect to the collector. This allowed us to obtain 125 µm-thick membranes with less than 30 µm variation in thickness over a surface of 20 x 30 cm.

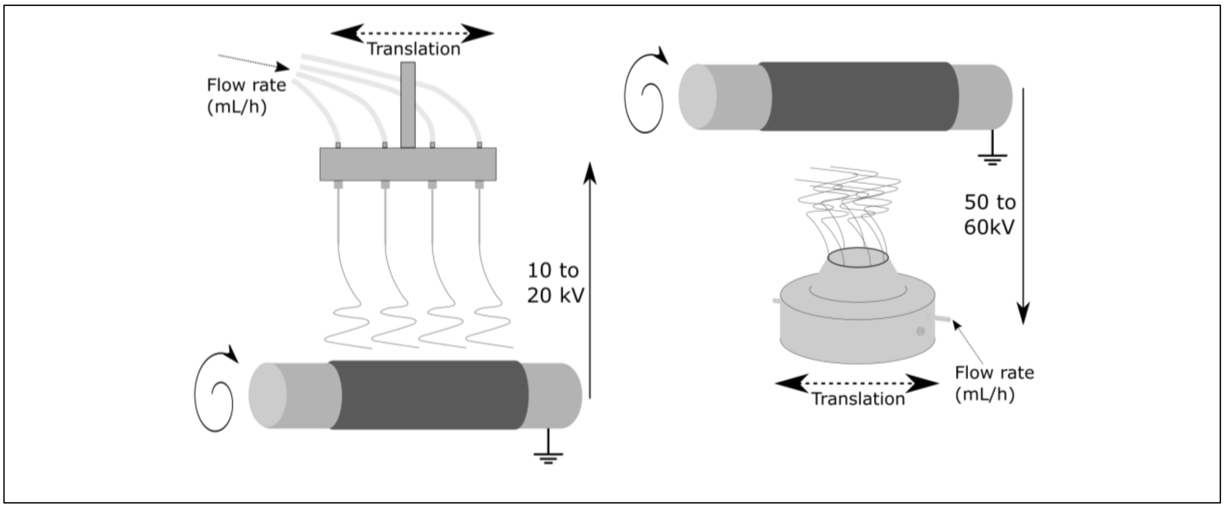

Figure 1: Electrospinning with a four needles emitter (left) and annular emitter (right)

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SURFACE COLOR ON DEMAND: Chameleon Effect

Karine MOUGIN[1], Feriel GHELLAL[1], Quentin BAUERLIN[1], Arnaud SPANGENBERG[1]

[1] Institut de Science des Matériaux de Mulhouse, Mulhouse, France
(corresponding author: karine.mougin@uha.fr)

ABSTRACT:

Colors affect our everyday life as they provide critical functions in both recognition and communication. Nearly all artifacts of our everyday are manufactured from polymers colored by dyes. This approach allows an endless variety of colors. And yet, **each individual item** is produced in **one** color, which cannot be changed after its production. This is a serious problem for manufacturers, as some goods cannot be sold anymore when their color is outdated. This issue can also cause **tremendous costs** and **waste** if products cannot be recycled and have to be deposed. *So, it is of **high interest** to **add color-changing surfaces** to the portfolio of manufacturing.* In nature, changing colors are frequently observed in the animal's world for camouflage by misleading natural enemies or for courting by standing out from the environment. The most prominent examples are chameleons that are able to exhibit complex and rapid color changes during social interactions due to dispersion/aggregation of pigment within dermal chromatophores. A direct copy nature is not typically practical for everyday items but is **the inspiration of our approach to create color change in polymeric material [1].**

The idea was to create a novel hybrid material able to color change of surfaces at will. The key element of this novel technology is based on plasmonic. The developed functional nanomaterial is composed of colloidal metallic nanoparticles (NPs) that are properly synthesized and assembled into matrix to ensure a variety of plasmonic colors under mechanical stresses. **By changing height and width of a polymer film and/or the size of nanostructures through the shape memory effect, the distance between the nanoparticles are modified inducing a color change in the composite material [2].**

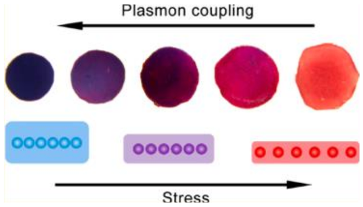

Figure 1: Basic principle of a colorimetric stress memory sensor developed by Han et al. [2]. Gold nanoparticle chains embedded in a polymer matrix. Applying stress to the film increases the distance of the gold nanoparticles resulting in a color change of the sample. (Reproduced from [1])

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Metal-oxide (MO) thin films obtained by laser curing: their integration in devices for opto-electronics.

Laurent Noël[1,2], **Dominique Berling** [1,2], **Hsiao-Wen Zan** [3], **Olivier Soppera** [1,2]

[1] Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France
[2] Université de Strasbourg, France
[3] Institute of Electro-Optical Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwn
(corresponding author: Olivier.soppera@uha.fr)

ABSTRACT:

Metal-oxide (MO) materials are transparent in the visible range, chemically inert, have good mechanical properties and high refractive indices. Their integration in devices for optics, photonics and micro-electronics is therefore widely developed[1]. Different processes can be used to prepare MO thin films, but the sol-gel route represents the lowest cost technique with a high degree of versatility, regarding the chemical composition and the resulting optical properties. However, temperatures between 300°C and 600°C are required to cure such materials and thus, limiting their integration on polymeric and other low thermal resistance substrates. Here, we present an alternative curing method developed by our team[2,3], based on Deep-UV (DUV) and near-infrared (NIR) irradiation.

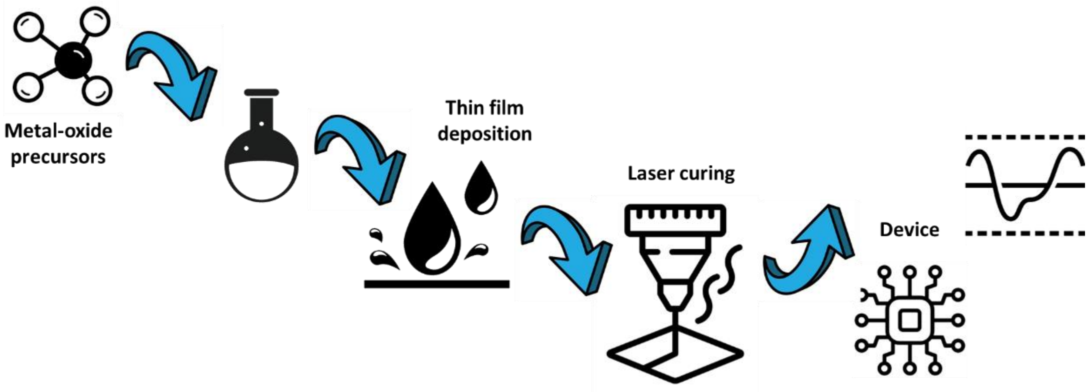

Figure 1: Schematic of thin films obtained by laser curing from MO precursors

Particularly, metal-oxide materials such as TiO_2 and ZrO_2 had been integrated in a plasmonic sensor made of plastic optical fibers (POF), in order to improve the performances regarding the sensitivity[4]. Among other devices, the integration of indium-doped zinc oxide (IZO) thin films was also performed on carbon composite to monitor the mechanical constraints. It could prevent a potential breakage of some protective equipment in sport activities…

In summary, this poster demonstrates the high versatility of the sol-gel route combined with laser curing, to design a wide range of sensors.

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DEVELOPMENT OF BIODEGRADABLE SELF-ROLLED PATCHES FOR DRUG RELEASE

Sidzigui OUEDRAOGO[1], Mathilde GROSJEAN[2], Arnaud PONCHE[1], Laurent PIEUCHOT[1], Valeriy LUCHNIKOV[1], Noëlle MATHIEU[3], Benjamin NOTTELET[2], Karine ANSELME[1]
[1] UMR 7361/UHA, Institut de Science des Matériaux de Mulhouse (Biomatériaux-Bio-interfaces), Mulhouse, France ;
[2] UMR 5247, Institut des Biomolécules Max Mousseron (Polymères pour la santé et les biomatériaux), Montpelier, France ;
[3]Institut de Radioprotection et de Sûreté Nucléaire (Laboratoire de radiologie des expositions médicales), Paris, France
Sidzigui.ouedraogo@uha.fr

A specific innovative treatment is needed to address the Pelvic Radiation Disease (PRD) [1,2]. Current treatments are symptomatic and not curative while some, like systematic drugs, induce systematic side effects. To achieve an efficient therapeutic solution and minimize systemic toxicity, a specific local treatment targeting the inflamed mucosa areas is proposed. We develop a biodegradable self-rolled patch that could be applied locally by colonoscopy without surgery. This innovative biomaterial is based on the combination of biodegradable hydrogel and elastomeric layers (Fig. 1A). The association of two different layers confers tunable mechanical and bio-resorption properties to the patch and allows the unidirectional release of anti-inflammatory drugs (AI) such as Budesonide and Prednisolone toward the ulcerated zone after its unrolling. Here we report the patch building methodology and his characterization. The similar nature of the two layers leads to a good cohesion and the formation a regular stable patch (Fig. 1B). The bilayer films are able to enroll (Fig. 1C) and achieve our final requirements (Fig. 1D). Ongoing work focuses on the optimization of amount of drug released and the patch self-unrolling to facilitate his deployment after the placement in the colon *in vivo*.

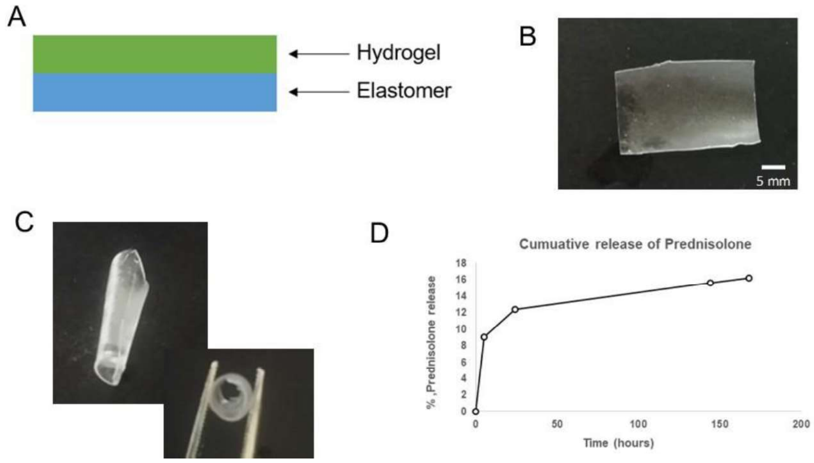

Figure 1: A- Schematic illustration of bilayer patch structure model. B- Synthetized drug delivery system (30 mm × 15 mm × 0.16 mm), C-PEG-PLA bilayer self-rolled tube 4 mm diameter. D-Cumulative release of Prednisolone from synthetized hydrogel layer

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SYNTHESIS OF 3-AMINO-5-FLUOROALKYLFURANS BY INTRAMOLECULAR CYCLIZATION.

Clotilde Plaçais[1], Morgan Donnard[1], Armen Panossian[1], Jean-Pierre Vors[2], David Bernier[2], Sergii Pazenok[3], Frédéric R. Leroux[1]

[1]Université de Strasbourg, Université de Haute-Alsace, CNRS, UMR 7042-LIMA, ECPM, 25 Rue Becquerel, Strasbourg 67087, France

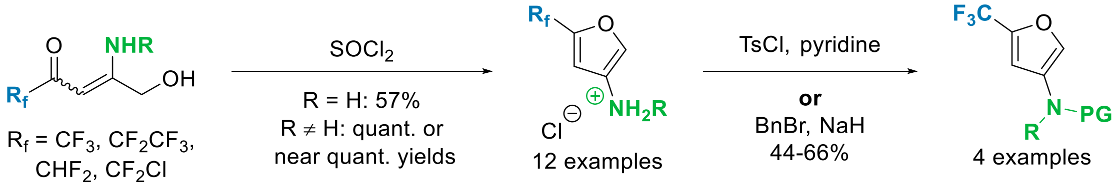
[2]Bayer S.A.S., 14 Impasse Pierre Baizet, BP99163, 69263 Lyon Cedex 09, France

[3]Bayer CropScience AG, Alfred-Nobel-Strasse 50, 40789 Monheim, Germany

ABSTRACT:

Furans are important structures in organic chemistry as intermediate in synthesis, and can be found in natural molecules or in pharmaceuticals and pesticides. Adding fluorine to those structures can enhance their biological properties, or for example render them more stable in acidic conditions, thanks to the electro attracting properties of this atom.[1] Furans bearing amino groups are also important precursors in agrochemistry and pharmaceutics.[2] However, fluorinated amino-furans are still scarcely described, in particular fluorinated 3-aminofurans, which are reported as more stable than those bearing an amino group in the 2 position.

In this communication, we will present the synthesis of 3-amino-5-fluoroalkylfurans by intramolecular cyclization of fluoroenones.[3] The furans are obtained in excellent yields, and the methodology is compatible with 4 different fluorinated groups and tolerates a variety of substituents on the amine. Protection of the amine allows to stabilize those furans and to widen the scope.



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Au nanoparticles/InZnO thin film prepared by laser annealing for wide range photodetector applications

Ching-Fu Lin[1,2,3], Amine Khitous,[1,2] Laurent Noel, [1,2] Hsiao-Wen Zan,[3]
Olivier Soppera[1,2]

[1] Université de Haute-Alsace CNRS, IS2M UMR 7361
Mulhouse 68100, France
[2] Université de Strasbourg, Strasbourg, France;
[3] National Yang Ming Chiao Tung University, Hsinchu, 300, Taiwan, ROC
(corresponding author: olivier.soppera@uha.fr)

ABSTRACT:

The development of alternative methods of integrating electronic devices has become a major issue in the context of the Internet of Things (IoT). Among these basic components, photodetectors are important devices for applications in health, sports or more generally sensors.

We propose a new method for preparing gold nanoparticles (Au NPs)/indium-zinc-oxide (IZO) nanocomposite thin films based on photothermal mechanisms with near-Infrared (NIR) laser-annealing, which allows integrating the nanomaterial on fragile substrates such as thin glass, plastic sheets, or 3D printed pieces. The Au NPs were first prepared by NIR laser dewetting of a thin Au layer. Then, the Au NPs were used to locally cure the semiconductor material and provide suitable electronic properties owing to their efficient thermoplasmonic effects under our NIR laser annealing conditions. Finally, the electronic properties of the Au NPs/IZO thin films were characterized in the dark and under light excitation. Good photoresponsivity at 410 nm (UV, > 10^0 A/W) was demonstrated, but interestingly, the presence of Au NPs significantly improved the detection ability to a longer wavelength range, such as to 515 nm (green, ~ 5×10^{-3} A/W), even extending to 630 nm (red, ~ 5×10^{-4} A/W), and 780 nm (NIR, ~ 10^{-4} A/W). In addition, with the critical evaluation of dynamic light detection and lifetime trace (> 22 days), the laser-annealed Au NPs/IZO photodetector (PD) demonstrated useful operating reliability and stability.

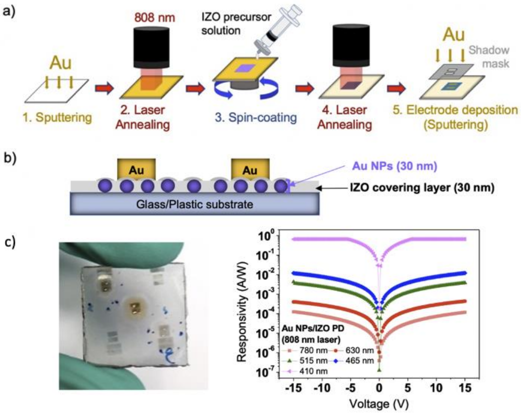

Figure 1 : a) Schematic view of the Au/IZO nanocomposite thin film preparation by laser annealing, b) Schematic view of the photodetector structure, c) Example of device on polymer substrate and photoresponse curves from UV to NIR.

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Biosourced photoresist for Deep-UV photolithography

Olha Sysova,[1,2,3] Paule Durin,[3,4] Thierry Delair,[5] Yann Chevolot,[3] Jean-Louis Leclercq,[3] Didier Leonard,[4] Dominique Berling, [1,2,] Olivier Soppera[1,2]

[1] Université de Haute-Alsace CNRS, IS2M UMR 7361
Mulhouse 68100, France
[2] Université de Strasbourg, Strasbourg, France;
[3] Univ Lyon, CNRS, Ecole Centrale de Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69134 Ecully Cedex, France
[4] Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, 69100 Villeurbanne, France
[5] Université de Lyon 1, Polytech, UMR-CNRS 5223, Ingénierie des Matériaux Polymères, F-69622, Villeurbanne
(corresponding author: olivier.soppera@uha.fr)

ABSTRACT:

Industrial resists and solvents for their synthesis are known for their toxicity and destructive influence on the environment. The new tendency in the industry is to switch to bio-sourced resists and eco-responsible processes[1,2]. Biosourced polymers are great candidates to replace industrial resists as they are non-toxic, water-soluble and biodegradable. In this study we focus on chitosan, which being uncommon in nature, is generally prepared by deacetylation of chitin, the second most abundant biopolymer on Earth after cellulose. Chitosan is a linear copolymer composed of monomeric units of D-glucosamine (or 2-amino-2-deoxy-D-glucopyranose) and N-acetyl-D-glucosamine (or 2-acetamido-2-deoxy-D-glucopyranose) These monomers are linked together by β-(1-4) glycosidic bonds.

This polysaccharide has a good potential since it forms homogeneous films that adhere well to the substrate. Moreover, it is intrinsically photosensitive under Deep-UV light (at 193 nm). Consequently, photopatterning can be achieved without any chemical modification of the polymer and development can be achieved by use of deionized water.

Different techniques were used to investigate the interaction of chitosan and deep-UV, such as: FTIR spectroscopy, XPS, ToF-SIMS, ellipsometry and SEC analysis. Based on these results we proposed a mechanism to explain the solubility change upon the irradiation which enables photopatterning on the polymer film.

Chitosan-based resist allows one to obtain micrometric features and followed by etching step shows its potential to be used in photolithography-based processes.

Examples of the patterns and etched structures are given in Fig. 1.

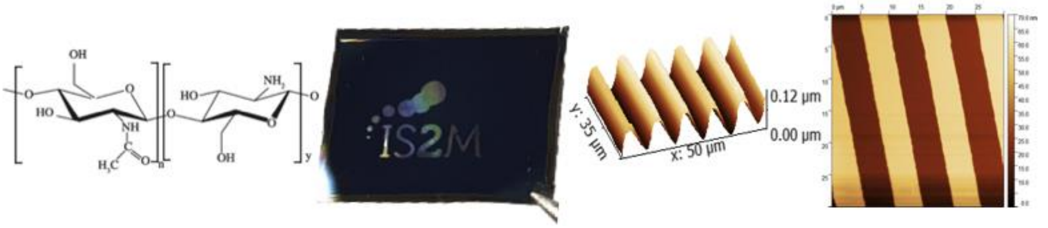

Figure 1 : Molecular structure of chitosan, examples of patterns obtained by DUV photolithography and after transfer by reactive ion etching (AFM).

Electrical characterizations of individual supramolecular crystals at the local scale

Joan Teyssandier,[a] Ludovic Josien,[a] Emmanuel Denys,[a] Jiang Jing,[b] Emilie Steveler,[b] Nicolas Leclerc,[c] Thomas Heiser[b] and Laurent Simon[a]

[a]Institut de Sciences des Matériaux de Mulhouse, CNRS-UMR 7361, Université de Haute Alsace, 3b rue Alfred Werner, Mulhouse, 68093 France. Email: joan.teyssandier@uha.fr
[b]Laboratoire ICube, UMR 7357, 23 rue du Loess, BP20, Strasbourg Cedex 2, France.
[c]Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, 25, rue Becquerel 67087 Strasbourg Cedex 2, France

Abstract:

The development and improvement of organic electronic devices requires analytical tools allowing for a deep understanding of the physical properties of the materials they are made of. Bulk characterization techniques only offer ensemble-averaging information that does not take into account the heterogeneity of the samples (defects, polymorphism, grain boundaries in polycrystalline materials, anisotropy…). The fabrication of devices on every region of interest of a sample is an extremely tedious and time consuming task. There is therefore a need for developing tools to probe locally the materials. In order to study the structure-property relationship, it is also important for these tools to be adaptable to other characterization techniques allowing correlative measurements.

In this contribution, the use for electrical measurements of a nanoprobing station consisting of four IMINA® nanorobots will be presented. The nanorobots can be equipped with tungsten tips that can thus be manipulated to contact any location of a sample at will, with a precision down to 10 nm. A proof-of-concept will be given by the study of supramolecular crystals of a thienopyrroledione (TPD) - triazatruxene (TAT) derivative (figure 1a), a molecule used in photovoltaics [1]. The probes are used in the environment of a scanning electron microscope (SEM) to contact on demand single crystals in various configurations (field-effect transistors, 4-probe measurements) to measure the electrical properties (such as mobility) of individual supramolecular objects. The possibilities of development for other types of materials and in other environments will be discussed.

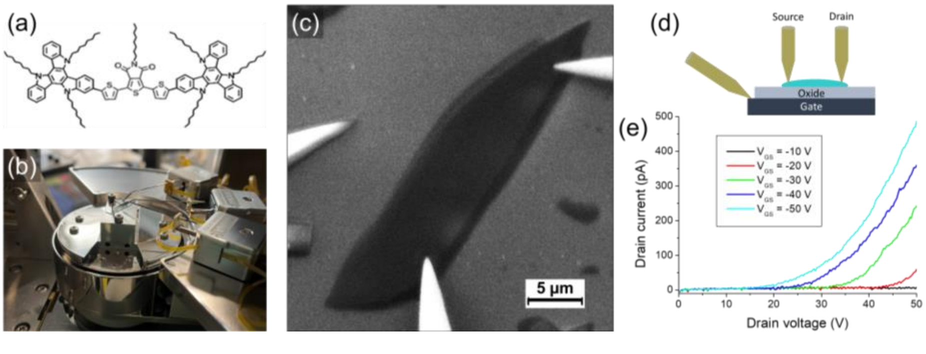

Figure: (a) structure of the TPDC8-TATC8 molecule; (b) photograph of the nanoprobing stage equipped with three robots and a sample placed on a cryo/heating module (range: -190°C to +300°C); (c) SEM image of a TPDC8-TATC8 supramolecular crystal contacted by two probes (source and drain); (d) diagram of experimental setup using three probes in a back-gate FET configuration; (e) output characteristic of a TPDC8-TATC8 crystal.

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Thionolactone as Resin Additive to Prepare (bio)degradable 3D Objects via VAT Photopolymerization

Constance Thomas,[1,2] Rana Mhanna,[1,2] Noémie Gil,[3] Jean-Pierre Malval,[1,2] Jean-Louis Clément,[3] Didier Gigmes,[3] Catherine Lefay,[3] Yohann Guillaneuf,[3] Olivier Soppera[1,2]

[1] Université de Haute-Alsace CNRS, IS2M UMR 7361
Mulhouse 68100, France
[2] Université de Strasbourg, Strasbourg, France;
[3] Aix-Marseille Univ., CNRS, Institut de Chimie Radicalaire (UMR 7273), Marseille, France
(corresponding author: olivier.soppera@uha.fr)

ABSTRACT:

3D printing and especially VAT photopolymerization leads to cross-linked materials with high thermal, chemical and mechanical properties. Nevertheless, such stability is incompatible with degradability and re/upcyclability. We showed here that thionolactone and especially dibenzo[c,e]-oxepane-5-thione (DOT) could be used as an additive (2 wt%) to acrylate-based resins to introduce weak bonds into the network via a radical ring-opening polymerization process. The low amount of additive allows to only slightly modify the printability of the resin, keep intact its resolution and maintain the mechanical properties of the 3D object. The resin with additive was used in UV microfabrication and 2-photon stereolithography setup and commercial 3D printers. The fabricated objects were shown to degrade in basic solvent as well in a home-made compost. The rate of degradation is nonetheless dependent of the size of the object. This feature was used to prepare 3D objects with support structures that could be easily solubilized.

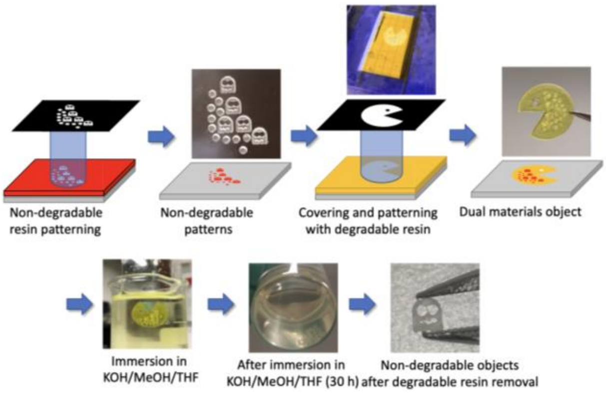

Figure 1 : Embedding a non-degradable object in the degradable resin: example of a degradable Pacman head containing ghosts and balls that are non-degradable.

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One-step Production of Polyelectrolyte and Charges Nanoparticles

Madeline Vauthier [1] **, Christophe A. Serra** [1]
[1] *Université de Strasbourg, CNRS, ICS UPR 22, F-67000 Strasbourg, France*

ABSTRACT:

Producing smaller and smaller neutral nanoparticles becomes a trend which main motivation is to diversify their application fields, such as drug delivery, biosensing or environmental research. However, charged and biphasic polymeric nanoparticles (NPs) did not yet find such success mainly due to the multi-step and time-consuming conventional production route.[1]

We propose here, for the first time, to extend the emulsification-evaporation method to the one-step production of negatively charged and Janus polymeric NPs. In this purpose, we used various processes (rotor-stator mixing, sonication and elongational-flow micromixing) to investigate the possible formation of poly(styrene sulfonate), PSS, NPs or NPs with a hydrophobic domain (poly(lactic-co-glycolic acid), PLGA) and a hydrophilic charged domain of PSS. We were thus able to control the particles' sizes, ranging from 30 to 400 nm, and we found that only the elongational-flow micromixer allowed the production of Janus-like NPs (Figure 1). Moreover, playing on PSS/PLGA mass ratio allowed to control the particles' shape, from Janus to core-shell structure.[2]

As a conclusion, we highlighted very interesting results concerning the controlled one-step production of monomodal charged particles which size can be tuned only by varying process parameters and with shape that can be tuned by varying chemical parameters.

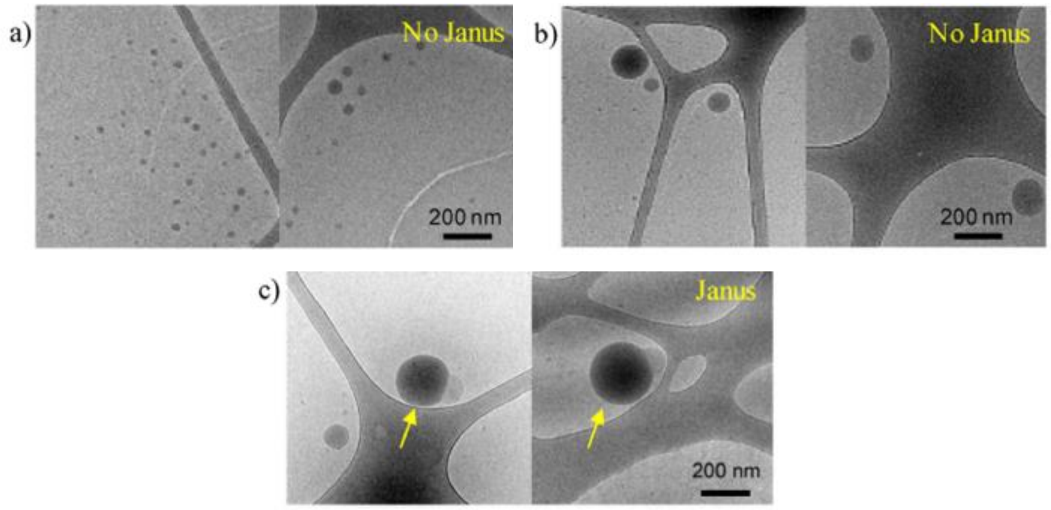

Figure 1 : Cryo-TEM images of PSS/PLGA nanosuspensions obtained with a) ultrasonicator, b) rotor-stator mixer and c) elongational-flow micromixer.[2]

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Nb, N CO-DOPED TiO$_2$ NANOPARTICLES FOR BROAD SPECTRUM SOLAR LIGHT ACTIVATION PHOTOCATALYSIS

Qingyang Xi[1], **Thomas Cottineau**[1], **Valérie Keller**[1]

[1] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES) - CNRS : UMR7515, université de Strasbourg, 25 rue Becquerel - 67087 Strasbourg Cedex 2 - France
(Thomas Cottineau: cottineau@unistra.fr)

ABSTRACT:

TiO$_2$ photocatalyst co-doped with Nb and N (Nb,N:TiO$_2$) were synthesized via a sol-gel method followed by a post thermal nitridation in ammonia atmosphere. The photocatalytic performance of Nb,N:TiO$_2$ was evaluated by conducting the photo-degradation of methylene blue (MB) solution under the irradiation of UV light or visible light and compared with TiO$_2$ and N doped TiO$_2$. Specific thermal condition of nitridation was found to significantly differentiate the photocatalytic activity of Nb,N:TiO$_2$. The result shows that proper thermal condition for N incorporation can elevate the level of charge compensation between Nb^{5+} and N^{3-}, leading to negligible formation of bulk defects and therefore strongly enhance the photocatalytic activity. However, over-intensive thermal condition of nitridation caused the generation of Ti^{3+} and oxygen vacancy in the bulk acting as charge recombination centre, resulting in the significant deterioration of photocatalytic performance. This study has emphasized the importance of understanding the complexity of the charge compensation scheme in the co-doped system, and that various defects can be introduced depending on the synthesis conditions. The photocatalytic performances in the UV and visible solar region then depend not only on the amount of cation and anion introduced, but also from the crystallographic nature of these introduced dopants in the lattice.

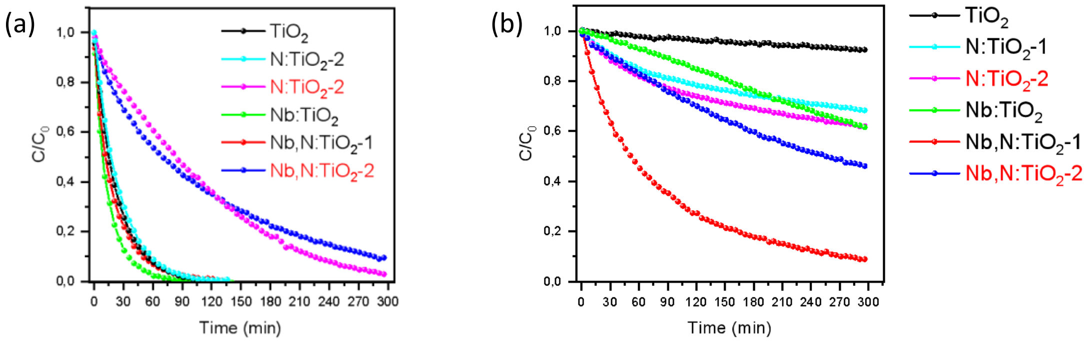

Figure 1: Degradation profile of MB under irradiation of (a) UV LED (365 nm) and (b) visible LED (450 nm)

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SYNTHESIS AND STUDIES OF OLEOGELS AS SUBSTITUTES FOR STRUCTURAL FATS

Senem Yilmazer[1], **Duncan Schwaller**[1], **Philippe Mesini**[1]

[1] *Université de Strasbourg, CNRS, Institut Charles Sadron, Strasbourg, France*
(corresponding author: mesini@ics-cnrs.unistra.fr)

ABSTRACT:

Trans-unsaturated fatty acids (TFA) in the diet represent a major public health problem because they increase the frequency of cardiovascular diseases. TFAs are present in many solid fats of animal origin or in margarines, resulting from the hydrogenation of vegetable oils. However, these solid fats are necessary to texture the lipid phases of food. In this context, many studies are being carried out to replace solid fats in foods. One of the most promising ways is to solidify *cis*-unsaturated oils (liquid at room temperature) by organogelators. These small molecules gel solvents at low concentrations, typically a few percent by weight,[1,2] self-assembling into a solid 3D network in oil. Organogelators capable of gelling edible oils are called oleogelators. Examples of oil gelators are easily found in the literature, but for food applications, they must be without adverse effects when taken orally. In the present work we have synthesized *N*-Palmitoyl-L-phenylalanine because this compound is endogenous i.e. naturally present in the body and we have tested it as gelators of rapeseed oil. We have studied the thermodynamic properties of the gels formed with it by micro differential calorimetry (μ-DSC), and their mechanical properties as a function of temperature. From these measurements, we mapped out the *c*-*T* phase diagram. This compound showed two polymorphs that correspond to two kinds of gels, and led to a gel-to-gel transition in addition to the classic sol-to-gel transition. The structures of both polymorphs have been investigated by cryo-SEM, WAXS, and FTIR, and were correlated with thermal and mechanical behaviour.

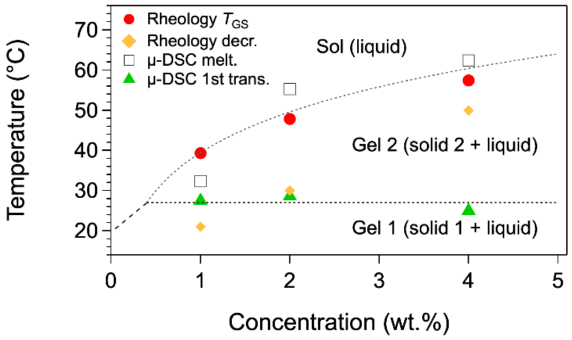

Figure 1: c-T phase diagram of Palmitoyl-L-phenylalanine/rapeseed oil; heating rate: 0.25 °C.min^{-1}

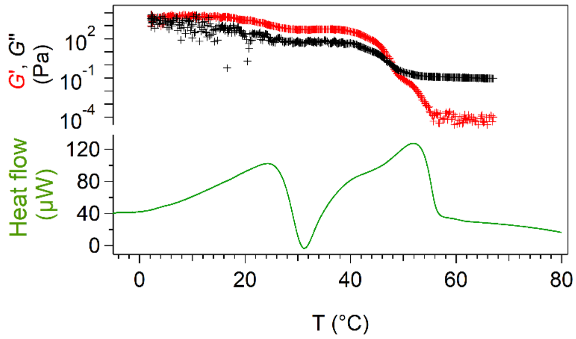

Figure 2: Elastic and viscous moduli of palmitoyl-L-phenylalanine/rapeseed oil (2 wt. %) as a function of T and thermograms upon heating (rate: 0.25 °C.min^{-1}).

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HIGH PERFORMING SUPERCAPACITOR COMBINING POROUS CARBON ELECTRODES AND A HYDROGEL ELECTROLYTE

Sirine Zallouz[1,2], **Jean-Marc Le Meins** [1,2], **Camélia Matei Ghimbeu** [1,2,3]

[1] Université Haute Alsace, CNRS, Institut de Sciences des Matériaux de Mulhouse (IS2M) UMR 7361, F-68100 Mulhouse, France
[2] Université de Strasbourg, F-67081 Strasbourg, France
[3] Réseau sur le stockage électrochimique de l'énergie (RS2E), FR CNRS 3459, 80039 Amiens Cedex, France
corresponding author: camellia.ghimbeu@uha.fr

Nowadays, commercial capacitors employ porous carbon as electrode with liquid electrolytes. Yet, these latter ones might present some leakage and corrosion issues. That is why much work is dedicated to search for alternatives such as gel and solid like electrolytes. They permit a good capacitor performance while suppressing these safety concerns at the same time. The good adhesion between porous carbon and gel electrolytes makes them good candidates for promising safe capacitors. In this context, developing a gel electrolyte to be used with porous carbon is an interesting strategy. In this work, chitosan is proposed as a low cost natural polymer to host KOH electrolyte via a simple synthesis method involving the cross-linking with glyoxylic acid. Then, by a drop cast technique the gel is formed and the chitosan-KOH gel electrolyte is cut in a circular shape (inset Fig. 1) and used with porous carbon.[1] The symmetric carbon capacitors show better performance than liquid 2 M KOH in some conditions. Moreover, the operational voltage window for this device can be extended until 1.3V with the alkaline chitosan-KOH gel electrolyte. The Ragone plot is calculated for the carbon capacitors using the gel electrolyte and liquid 2 M KOH at 0.8 and 1.3V and a considerable gain in the energy density can be seen at 1.3V (Figure 1). In addition to the energy density improvement the suppression of negative hazardous gas formation and liquid leakage is avoided. In a perspective, the chitosan-KOH gel electrolyte will be used with pseudocapacitive materials in order to achieve a high performance pseudocapacitor using an alkaline gel electrolyte.

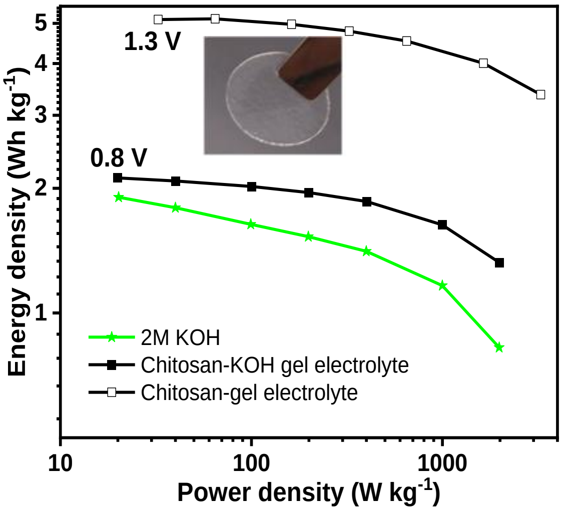

Figure 1: Ragone plot of Carbon/Carbon capacitors with chitosan-gel electrolyte and liquid 2M KOH electrolyte (inset) Photo of gel electrolyte cut and ready to insert in a two-electrode device

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