



Balard Chemistry Conferences

Materials for health, energy & environment

BOOK OF ABSTRACTS

15th-18th June 2021 | Montpellier - France

LabEx
CheMISyst

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The Balard chemistry Conferences - Presentation

This year, “Balard Conferences” honor materials and their applications in the fields of energy, environment and health. A great occasion to present the recent achievements performed within the four institutes of chemistry of Montpellier. All aspects will be covered, from the design and synthesis of materials and their precursors, to transformations into functional materials, as well as modelling and characterization.

Organized in Montpellier (ENSCM), from the 15th to the 18th of June 2021, our aim is to put into context the chemical society’s contributions to tackle the XXIst century challenges around the three main themes brought forward by the I-SITE MUSE: “to feed, to protect and to cure”. The event will also be accessible on **LIVESTREAMING** with a networking platform, for free, on <https://BALARD.LIVE> !

Since 2014, “Balard Conferences” are a privileged forum, where 250 academics and industrialists, including students and international experts, gather to foster scientific interactions, and to gain deeper insights around key research themes.

We welcome you to explore the different lectures and posters organized in 3 topics:



1. MATERIALS FOR **HEALTH**



2. MATERIALS FOR **ENERGY**



3. MATERIALS FOR **ENVIRONMENT**

Scientific Committee

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Guillaume MAURIN | ICGM
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Johanna BISMUTH | ENSCM
Héléa KHAIZOURANE | Pôle chimie

Guest Speakers

Florence BABONNEAU | Sorbonne University
Melinda DUER | University of Cambridge
Bruno CHAUDRET | INSA Toulouse - French Academy of Sciences
Georges HADZIIOANNOU | University of Bordeaux
Antoine MAIGNAN | Normandy University
Roland PELLENG | George Washington University
Patrice SIMON | Toulouse III University - French Academy of Sciences
Sandra VAN VLIERBERGHE | Ghent University

- PROGRAMME -

Amphi Mousseron

Amphi Mousseron

Amphi Godechot

Tuesday, June 15 th		Wednesday, June 16 th	
9:00	 <p>MUSE 2021 Balard Chemistry Conferences 15-18th June 2021 Montpellier (France)</p> <p>POLE CHIMIE MONTPELLIER UNIVERSITÉ D'EXCELLENCE</p> <p>Informations https://balard-conferences.fr</p> <p>Plateforme LIVE https://balard.live</p> <p>Contact contact@balard-conferences.fr</p> <p><i>On-site registrations</i></p> <p>Inauguration of "Pôle Chimie de MUSE"</p> <p><i>Break</i></p> <p>Balard Conferences OPENING</p> <p>GS01 - R. PELLENQ, George Washington University</p> <p>GS02 - M.DUER, University of Cambridge</p> <p><i>Poster session</i></p>	9:00	<p>GS03 - S.VAN VLIERBERGHE, Ghent University</p> <p>KN01 - ML.FOCARETE, University of Bologna</p> <p>OC01 - K. BELABBES, IBMM</p> <p>OC02 - W. WANG, IEM</p> <p>OC03 - T.BROSSIER, ICGM</p> <p>OC04 - J. CASSETTA, IEM</p> <p><i>Break</i></p> <p>KN02 - M.BARBOIU, CNRS</p> <p>OC05 - J. BEN GHOZI-BOUVRANDE, ICSM</p> <p>OC06 - L. DHELLEMES, IBMM</p> <p>OC07 - D. STRILETS, IEM</p> <p>OC08 - M. GROSJEAN, IBMM</p> <p>OC09 - A. FATNASSI, ICGM</p> <p>OC10 - Y. A. GUECHE, ICGM</p> <p><i>Lunch</i></p> <p>GS04 - G. HADZIOANNOU, University of Bordeaux</p> <p>KN03 - J. DAOU, University of Haute Alsace</p> <p>OC11 - K. ŚWIRK, ICGM</p> <p>OC12 - C. PECHBERTY, ICGM</p> <p>OC13 - H. BOUZIT, IEM</p> <p>OC14 - L. ABBASSI, ICGM</p> <p>OC15 - G. DAKROUB, IEM</p> <p>OC16 - K. ATA, ICGM</p> <p><i>Break</i></p> <p>KN04 - R. SEMINO, University of Montpellier</p> <p>OC17 - P. JUND, ICGM</p> <p>OC18 - M. FABBIANI, ICGM</p> <p>OC19 - N. TULEUSHOVA, IEM</p> <p>OC20 - G. EL CHAWICH, IEM</p> <p>OC21 - P. DA COSTA, Sorbonne Univ.</p> <p>OC22 - K. BUYUKSOY, IMT Mines Alès</p> <p>OC23 - C. OBERLIN, IEM</p> <p>OC24 - T. PELLUAU, ICGM</p> <p>OC25 - M. MAFFRE, ICGM</p> <p>OC26 - K. PÉREZ DE CARVASAL, IBMM</p>
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- PROGRAMME -

Amphi Mousseron

Amphi Godechot

Amphi Mousseron

Amphi Godechot

Thursday, June 17 th		Friday, June 18 th	
9:00		9:00	
9:15	GS05 - F. BABONNEAU, Sorbonne University	9:15	GS07 - P. SIMON, Toulouse III University
9:30		9:30	
9:45		9:45	OC53 - T. LALIRE, IMT Mines Alès
10:00	KN05 - N. STEUNOU, University of Versailles Saint-Quentin	10:00	OC54 - S. ALSAYEGH, IEM
10:15	OC27 - R. GUTIÉRREZ-CLIMENTE, IBMM	10:15	OC55 - Y. FOUCAUD, ICSM
10:30	OC28 - F. REN, IEM	10:30	OC56 - F. CUMINET, ICGM
10:45	OC29 - B. MEZGHRANI, IBMM/ICGM	10:45	OC57 - Y. HOLAË, IEM
11:00	OC30 - J. LIZION, ICGM	10:45	OC58 - R. OYE AUKE, ICSM
11:15	Break	11:00	Break
11:30	KN06 - F. CUNIN, CNRS	11:00	OC59 - L. DESMURS, ICGM
11:45	OC31 - T. AUBERT, ICGM	11:15	OC60 - M. SEMSARILAR, IEM
12:00	OC32 - K. WANG, ICSM	11:15	OC61 - P. LACROIX-DESMAZES, ICGM
12:15	OC33 - L. SIMON, ICGM	11:30	OC62 - Q. WANG, ICGM
12:30	OC34 - S. LARBAOUI, ICGM	11:30	OC63 - S. LEMOUZY, ICGM
12:45	OC35 - C. BAROU, IEM	11:45	OC64 - S. ALDROUBI, ICGM
13:00	OC36 - G. FOLARANMI, IEM	11:45	Award ceremony of the best poster
13:15		12:00	
13:30	Lunch	12:15	GS08 - B. CHAUDRET, INSA Toulouse
13:45		12:30	
14:00		12:45	Balard Conferences CLOSING
14:15	GS06 - A. MAIGNAN, Normandy University	13:00	 <p>Health session</p>
14:30		13:15	
14:45	KN07 - C. CHANEAC, Sorbonne University	13:30	
15:00		13:45	 <p>Environment session</p>
15:15	OC37 - Q. HANNIET, IEM	14:00	
15:30	OC38 - M. CAHU, ICGM	14:15	
15:45	OC39 - R. MIGHRI, ICGM	14:30	 <p>Energy session</p>
16:00	OC40 - A. SERHOUNI, IBMM	14:45	
16:15	OC41 - F. DUQUET, IEM	15:00	
16:30	OC42 - N. BONDON, ICGM	15:15	
16:45	Break	15:30	
17:00	KN08 - R. BERTHELOT, CNRS	15:45	
17:15		16:00	
17:30	OC43 - A. SZYMASZEK, AGH Univ.	16:15	
17:45	OC44 - S. DAAKOUR, IEM	16:30	
18:00	OC45 - K. B. CERVANTES DIAZ, IEM	16:45	
	OC46 - L. DARONNAT, ISEC	17:00	
	OC47 - B. QUIENNE, ICGM	17:15	
	OC48 - J. EL HAYEK, IEM	17:30	
	OC49 - J. SCHNEIDER, ICGM	17:45	
	OC50 - M. VINCENT, ICGM	18:00	
	OC51 - M. FANG, IEM		
	OC52 - E. GULCAY, ICGM		

p.13 GUESTS SPEAKERS LECTURES

- p.14 GS1 - Roland PELLENQ, George Washington University
Carbon-cement nano-composite electrodes: science and applications to reduce the ecological footprint of concrete by giving it new functionalities
- p.16 GS2 - Melinda DUER, University of Cambridge
Heavy mice and lighter things: using solid-state NMR to explore the structure of tissues in health and disease
- p.18 GS3 - Sandra VAN VLIERBERGHE, Ghent University
Versatile biomaterial platform: from photo-crosslinkable bioinks to shape memory polymers
- p.20 GS4 - Georges HADZIIOANNOU, University of Bordeaux
Solid-state electrocaloric cooling, from materials to devices
- p.22 GS5 - Florence BABONNEAU, Sorbonne University
Solid-State NMR: a powerful tool to characterize hydroxyapatites
- p.24 GS6 - Antoine MAIGNAN, Normandy University
(Magneto)thermopower and thermal conductivity in oxides and sulfides
- p.25 GS7 - Patrice SIMON, Toulouse III University
Electrochemistry at the nanoscale: understanding ion adsorption/transfer in electrodes for energy storage applications
- p.26 GS8 - Bruno CHAUDRET, INSA Toulouse
Organometallic nanoparticles for magnetically induced catalysis

p.31 KEYNOTES

- p.32 KN1 - Maria Letizia FOCARETE, University of Bologna
Functional 3D-nanofiber-hydrogel composites for biomedical applications
- p.34 KN2 - Mihail BARBOIU, CNRS
Artificial water channels-toward biomimetic membranes for desalination
- p.36 KN3 - Jean DAOU, University of Haute-Alsace
Zeolite as a major solution for molecular decontamination in space
- p.38 KN4 - Rocio SEMINO, University of Montpellier
Modelling of MOF/polymer composites: from compatibility to performance
- p.40 KN5 - Nathalie STEUNOU, University of Versailles Saint-Quentin
Design of porous composites by assembling MOFs with (bio)macromolecules or carbon based materials for environmental related applications
- p.42 KN6 - Frédérique CUNIN, CNRS
Porous silicon, a biodegradable semiconductor for nanomedicine
- p.44 KN7 - Corinne CHANEAC, Sorbonne University
Conceptual architectonic of luminescent nanoparticles for optical imaging and temperature sensing
- p.46 KN8 - Romain BERTHELOT, CNRS
Shuffling alkali ions in layered transition metal oxides: crystallochemistry challenge and possible applications

p.49 ORAL COMMUNICATIONS

- p.50 OC1 - Karima BELABBES, IBMM | *Design of hybrid peptide / polymer nanofibers for soft tissues regeneration*
- p.52 OC2 - Wensen WANG, IEM | *Covalent functionalized MoS₂ membranes with tunable layer spacing for molecular sieving*
- p.54 OC3 - Thomas BROSSIER, ICGM | *Hybrid polymer biomaterial for tissue engineering scaffold using stereolithography*
- p.56 OC4 - Jeanne CASSETTA, IEM | *Graphene oxide (Go) assisted polymeric hollow fibers membranes for water purification*
- p.58 OC5 - Justine BEN GHOZI-BOUVRANDE, ICSM | *Liquid porous nanomaterials for liquid-liquid extraction*
- p.60 OC6 - Laura DHELLEMMES, IBMM | *Optimizing intact protein separation using capillary electrophoresis*
- p.62 OC7 - Dmytro STRILETS, IEM | *Synergetic self-assembly of alkylureido systems into artificial water channels*
- p.64 OC8 - Mathilde GROSJEAN, IBMM | *Design of degradable elastomers and hydrogels for the conception of bioresorbable anti-inflammatory patches*
- p.66 OC9 - Asma FATNASSI, ICGM | *Carbon aerogels as catalysts supports for hydrogenation reactions of organic molecules*
- p.68 OC10 - Yanis A. GUECHE, ICGM | *Selective laser sintering of solid oral dosage forms with Copovidone and Paracetamol using a CO₂ laser*
- p.70 OC11 - Katarzyna ŚWIRK, ICGM | *Low-temperature selective catalytic reduction of NO by NH₃ over HKUST-1 catalysts impregnated with Mn*
- p.72 OC12 - Clément PECHBERTY, ICGM | *Alloys negative electrode for Mg-ion/S batteries*
- p.74 OC13 - Hana BOUZIT, IEM | *Synthesis and self-assembly of double stimuli-responsive polystyrene-block-poly(2-vinylpyridine)-block-poly(N-isopropylacrylamide) triblock terpolymers*
- p.76 OC14 - Linda ABBASSI, ICGM | *Cumulative effects of stacking faults and nanostructuring on thermoelectric properties of β-FeSi₂*
- p.78 OC15 - Ghadi DAKROUB, IEM | *Organosilicon PECVD films for BTEX gases detection*
- p.80 OC16 - Karima ATA, ICGM | *Crystallographic and DFT investigation of weak CH...O hydrogen bonds in as-synthesized zeolitic materials*
- p.82 OC17 - Philippe JUND, ICGM | *Defects and their influence on the thermoelectric properties of materials: an ab initio study*
- p.84 OC18 - Marco FABBIANI, ICGM | *Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica*
- p.86 OC19 - Nazym TULEUSHOVA, IEM | *Au and Au-Ag electrocatalysts for glycerol oxidation and co-production of hydrogen*
- p.88 OC20 - Ghenwa EL CHAWICH, IEM | *3D printing of a new generation of structured polymer derived ceramics*
- p.90 OC21 - Patrick DA COSTA, Sorbonne University | *CO₂ methanation over V-promoted hydrotalcite-derived nickel catalysts for CO₂ methanation: on the effect of the catalyst preparation method*

- ABSTRACTS | SUMMARY -

- p.92 OC22 - Kubra BUYUKSOY, IMT Mines Alès | *Improvement of mechanical and microstructure of poly(lactic acid) based blends for biomedical applications*
- p.94 OC23 - Cyril OBERLIN, IEM | *Elaboration of silica ceramics by indirect additive manufacturing and aqueous gelcasting*
- p.96 OC24 - Tristan PELLUAU, ICGM | *Encapsulation of bio-inspired Mn complexes in mesoporous silica nanoparticles with improved biocompatibility for the regulation of oxidative stress*
- p.98 OC25 - Marion MAFFRE, ICGM | *Chemical and electrochemical processes in "Water-in-salt" electrolyte*
- p.100 OC26 - Kévan PÉREZ DE CARVASAL, IBMM | *Folding of phosphodiester-linked donor-acceptor oligomers into supramolecular nanotubes in water*
- p.102 OC27 - Raquel GUTIÉRREZ-CLIMENTE, IBMM | *Biomimetic protein imprinting on magnetic particles using amino acid-based hybrid blocks*
- p.104 OC28 - Feilhong REN, IEM | *Artificial nucleation sites and the study of solvation structures in electrolytes for Lithium metal batteries*
- p.106 OC29 - Braham MEZGHRANI, ICGM/IBMM | *Light Photodynamic Therapy and Photochemical Internalization of siRNA*
- p.108 OC30 - Juliette LIZION, ICGM | *¹²⁵Te NMR structural investigations coupled to NMR shift prediction suitable for Te containing Crystalline Materials*
- p.110 OC31 - Tangi AUBERT, ICGM | *Cage-derived mesoporous silica nanomaterials*
- p.112 OC32 - Kunyu WANG, ICSM | *Analysis of ion correlation in silica nanochannels: Molecular Dynamics of ion distribution and Potential of Mean Force*
- p.114 OC33 - Laurianne SIMON, ICGM | *Polyoxazolines nanoformulations towards an effective antioxidant delivery to prevent skin cancer*
- p.116 OC34 - Salima LARBAOUI, ICGM | *Iron and/or titanium containing microporous Silico-aluminophosphates as a novel photocatalyst for hydrogen production by water splitting process.*
- p.118 OC35 - Carole BAROU, IEM | *Fabrication of injectable calcium phosphate cements containing polymer microspheres for drug delivery*
- p.120 OC36 - Gbenro FOLARANMI, IEM | *Influence of NaCl concentration on the Desalination Performance of carbon based Flow Electrode.*
- p.122 OC37 - Quentin HANNIET, IEM | *Si(B)CN/ rGO composites as an electrocatalyst for Hydrogen Evolution Reaction (HER)*
- p.124 OC38 - Maëlle CAHU, ICGM | *A systematic rational study of the influence of the insertion of Mn²⁺ in Prussian blue nanoparticles on their photothermal properties*
- p.126 OC39 - Rimeh MIGHRI, ICGM | *REVERSIBLE H₂ storage via BCN*
- p.128 OC40 - Alexandra SERHOUNI, IBMM | *Development of novel strategies to target DNA methylation and histone acetylation in cancers*
- p.130 OC41 - Fanny DUQUET, IEM | *3Modified titanium oxide for green hydrogen production by electro-photocatalysis*
- p.132 OC42 - Nicolas BONDON, ICGM | *Nanodiamond-based organosilica nanoparticles for two-photon imaging and antibacterial photodynamic therapy*
- p.134 OC43 - Agnieszka SZYMASZEK, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY | *Catalytic activity of natural clinoptilolite and MWW-type zeolite modified with iron in selective catalytic reduction of nitrogen oxides with ammonia (NH₃-SCR)*

- ABSTRACTS | SUMMARY -

- p.136 OC44 - Sanaa DAAKOUR, IEM | *Dynamer-liposome dynamic system for drug delivery*
- p.138 OC45 - Karla B. CERVANTES-DIAZ, IEM | *Design of mesoporous SiC membranes from polymeric precursors for water filtration*
- p.140 OC46 - Loïc DARONNAT, ISEC | *What news on the plutonium-calmodulin variants interaction at molecular scale?*
- p.142 OC47 - Baptiste QUIENNE, ICGM | *Enhanced aminolysis of cyclic carbonates by β -hydroxyamines for the production of fully biobased polyhydroxyurethanes*
- p.144 OC48 - Joelle EL HAYEK, IEM | *Synthesis, functionalization and 3D printing of bioceramics for bone engineering*
- p.146 OC49 - Julien SCHNEIDER, ICGM | *Polyacid-functionalized mesoporous materials : synthesis and evaluation of the performances in heterogeneous catalysis*
- p.148 OC50 - Maxime VINCENT, ICGM | *In vitro and in vivo evaluation of antioxidant formulations to treat Macular Degeneration*
- p.150 OC51 - Mingyuan FANG, IEM | *CPolymer assisted MOF synthesis and membrane preparation*
- p.152 OC52 - Ezgi GULCAY, ICGM | *From High-throughput Computational Screening to Experimental Validation for Siloxane Adsorption in MOFs*
- p.154 OC53 - Thibaut LALIRE, IMT Mines Alès | *Chemical modification impact of graphene or graphite in conductive nanocomposite morphology control*
- p.156 OC54 - Syreina ALSAYEGH, IEM | *Design of advanced photocatalytic materials by atomic layer deposition (ALD)*
- p.158 OC55 - Yann FOUCAUD, ICSM | *Hydration mechanisms of uranium dioxide (UO₂): new insights from ab initio molecular dynamics simulations*
- p.160 OC56 - Florian CUMINET, ICGM | *Catalyst-free transesterification vitrimers: the power of fluorine to activate bond exchanges*
- p.162 OC57 - Yaovi HOLADE, IEM | *Designed catalytic nanostructures for the biomass electro-reforming in membrane electrolyzers*
- p.164 OC58 - Ruth OYE AUKE, ICSM | *Synthetic methodologies and study of thermosetting resins obtained from biobased and/or non-toxic compounds for the recovery of critical metals*
- p.166 OC59 - Lucie DESMURS, ICGM | *Determination of porous surfaces and volumes in mesoporous zeolites for catalytic valorization of methylmercaptan*
- p.168 OC60 - Mona SEMSARILAR, IEM | *Preparation of well-defined 2D-lenticular aggregates by self-assembly of PNIPAM-*b*-PVDF amphiphilic diblock copolymers in solution*
- p.170 OC61 - Patrick LACROIX-DESMAZES, ICGM | *Polymer-assisted supercritical CO₂ extraction of Pd from supported catalysts: a step toward green recycling of precious metals*
- p.172 OC62 - Qing WANG, ICGM | *First evidence of size-dependence on structure transition of gold nanoparticles under H₂ by combined in situ HRTEM and AIMD simulations*
- p.174 OC63 - Sébastien LEMOUZY, ICGM | *Understanding the synthesis and reshaping of fluorinated polyester vitrimers: a kinetic study*
- p.176 OC64 - Soha ALDROUBI, ICGM | *Task-specific ionic liquids for the synthesis of functional carbonaceous materials*

- POSTERS SESSION -

A digital poster session is also available on balard.live.
Enjoy the short videos which summarise each poster presented in the list!

Energy

- PC1/ **Martin DROBEK**, IEM - Synergistic effect of Pd nanoparticles and mof membranes on nanowires hydrogen sensors
PC2/ **Mathilde DUFOUR**, ICGM - Synthesis of new π -conjugated molecules for organic solar cells
PC3/ **Jordan GARO**, ICGM - π -conjugated materials from biosourced precursors
PC4/ **Elizabeth MAKOMBE**, ICSM - Malonamides for the multi-recycling of nuclear spent fuel
PC5/ **Aydin OZCAN**, ICGM - How MOF/polymer interfacial void shape/size affect the gas permeability of mixed matrix membranes
PC6/ **Ludvine POYAC**, ICGM - Catalytic properties of porphyrins bearing peripheral n-heterocyclic carbene rhodium complexes
PC7/ **Kiran TAKSANDE**, ICGM - Exploration of guest@MOFs as proton conductors
PC8/ **Qing WANG**, ICGM - Stability of Pt-single atom catalysts (saas) dispersed in transition-metal surfaces under hydrogen pressure at various temperatures
PC9/ **Huali WU**, IEM - Enhancing the C^{2+} production from the electrochemical reduction of CO_2 using functionalization

Environment

- PC10/ **Shadi AL-NAHARI**, ICGM - Investigation of the more environment-friendly solvent-free approach for the syntheses of zeolites
PC11/ **Dimitri BERNE**, ICGM - Catalyst-free epoxy vitrimer based on transesterification internally activated by β -CF₃ group
PC12/ **Florian CUMINET**, ICGM - Catalyst-free transesterification vitrimers: the power of fluorine to activate bond exchanges
PC13/ **Dandan SU**, IEM - Polyamine dynamic frameworks as activators of carbonic anhydrases
PC14/ **Sophie HERR**, ICSM - Contribution of ultrasound in the depollution of heavy metals from vermiculite clay
PC15/ **Bonito KARAMOKO**, IEM - Nanocomposite membranes based on polymere/exfoliated 2D materials obtained by pickering emulsion
PC16/ **Céline POCHAT**, IEM - Open innovation test bed for nano-enabled membranes
PC17/ **Wael RMILI**, Sfax University, Tunisie - Study of mechanical properties of Reverse Osmosis (RO) membranes under operating conditions
PC18/ **Bamlak SETEGNE**, ICGM - Development of transparent bipolar membrane for photoelectrochemical conversion of CO_2
PC19/ **Agnieszka SZYMASZEK**, AGH University of Science and Technology, Poland - Natural clinoptilolite modified with iron or/copper as an effective catalyst of selective catalytic reduction of nitrogen oxides with ammonia (NH_3 -SCR)
PC20/ **Fida TANOS**, IEM - Calcium copper titanate based nanocomposites for the photoelectrocatalytic wastewater treatment

Health

- PC21/ **Laura ARSENIÉ**, ICGM - New nucleobase derived polymers for self-assembled DNA-inspired architectures
PC22/ **Nicolas BONDON**, ICGM - Nanodiamond-based organosilica nanoparticles for two-photon imaging and antibacterial photodynamic therapy
PC23/ **Maeva COSTE**, IBMM - Cell-selective siRNA delivery using glycosylated dynamic covalent polymers self-assembled in situ by RNA-templating
PC24/ **Bénédicté FROMAGER**, IEM - 3D membranes of electrospun fibers for cell therapies
PC25/ **Oumaima KARAI**, Sidi Mohamed Ben Abdellah University Fez, Morocco - Design, synthesis and biological screening of new heterocyclic carboxylic α,α -diaminoesters
PC26/ **Elodie LOGEROT**, IBMM - Amidated and carboxylated peptides mass spectrometric separation based on survival yield technique
PC27/ **Ilyes MAHTI**, ISEC - Chelation of zirconium by the dota ligand, a multiparametric study
PC28/ **Lucas MELE**, ICGM - Phosphorus based small molecules as promising lead candidate to alleviate NDs through modulation of S1R
PC29/ **Amina MERABTI**, ICGM - Photosensitizers targeting carbonic anhydrase for synergistic therapy of multiresistant hypoxic tumors
PC30/ **Youssef MOUACHA**, IEM - Synthesis, characterization and the antibacterial activity of a new [1.2.3] triazole derivative
PC31/ **Noelia SANCHEZ-BALLESTER**, ICGM - Alginate esters: novel multifunctional excipients for direct compression
PC32/ **Alexandra SERHOUNI**, IBMM - Development of novel strategies to target DNA methylation and histone acetylation in cancers



GUEST SPEAKERS



GS

Balard Chemistry Conferences - 15th-18th June 2021

Carbon-cement nano-composite electrodes: science and applications to reduce the ecological footprint of concrete by giving it new functionalities

GS1

Roland PELLENQ

roland.pellenq@cnr.fr

• EPIDAPO, LAB
GEORGE WASHINGTON UNIVERSITY
CHILDREN'S NATIONAL MEDICAL CENTER



Due to a significant ecological footprint during its manufacture (5 to 10% of industrial CO₂ emissions), cement faces an uncertain future. However, thanks to advances in the science and engineering of nano-composites, cement can today acquire new potential to contribute to sustainable development if, in addition to its intrinsic properties in terms of mechanical resistance, new functionalities (such as super-capacitor for example) were added to it allowing the structural elements of a building (beams, floors, etc.) to store electrical energy.

We report here the synthesis and characterization of a new family of nanoporous cement-carbon nano-composites, electron conductors and capable of storing electrical energy. First, the preparation of these materials and their electrically conductive properties will be discussed. A complete characterization of these materials has been carried out using a wide variety of experimental techniques. Finally, nano-indentation techniques are used to assess the mechanical properties (hardness, elasticity and creep modulus). Monte-Carlo Grand-Canon-type mesoscale simulations make it possible to understand the 3D-percolating distribution of carbon nanograins in the capillary pore network of the cement matrix.

Other applications of such an electronically conductive cement will also be mentioned, in particular concerning the development of water desalination units, the exploitation of the Joule effect and hydrophobicity for the protection of concrete with regard to freeze / thaw cycles.

Heavy mice and lighter things: using solid-state NMR to explore the structure of tissues in health and disease

GS2

Melinda DUER

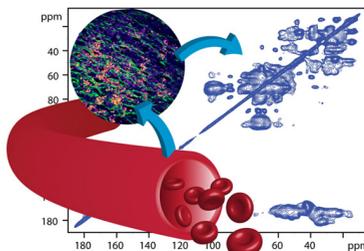
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Ageing and metabolic diseases causes tissue dysfunction, typically resulting in impaired mechanical properties and increased risk of, e.g. bone fracture and tendon rupture. Developing materials to repair tissue defects successfully requires detailed knowledge of the molecular structure of the mechanical component of the tissue, the extracellular matrix, as the goal of any tissue repair is an implant material that integrates completely with the existing tissue and promotes healthy cell function.

In this talk I will describe how we use solid-state NMR methods, integrated with confocal and electron microscopy, to understand the molecular structure of the extracellular matrix, how it interfaces with cells and how its structure changes in ageing [1] and under mechanical strain. Examples will include calcified tissues in both pathological and physiological contexts (vascular calcification [2] and bone [3]) and if time permits, cancer. I will argue that the extracellular matrix structure is instrumental in driving cell differentiation and phenotype, and further, that controlling the extracellular matrix structure is a potential therapeutic route in a number of diseases.



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Versatile biomaterial platform: from photo-crosslinkable bioinks to shape memory polymers

GS3

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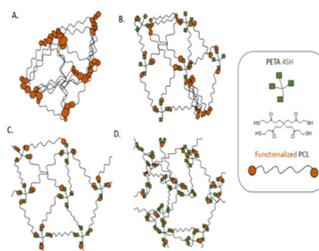
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Biofabrication is a specific area within the field of tissue engineering which takes advantage of rapid manufacturing (RM) techniques to generate 3D structures which mimic the natural extracellular matrix (ECM). A popular material in this respect is gelatin, as it is a cost-effective collagen derivative, which is the major constituent of the natural ECM. The material is characterized by an upper critical solution temperature making the material soluble at physiological conditions. To tackle this problem, the present work focusses on different gelatin functionalization strategies which enable covalent stabilization of 3D gelatin structures [1,2].

In a second part, synthetic acrylate-endcapped, urethane-based precursors (AUP) based on polyethers and polyesters, will be discussed with exceptional crosslinking behaviour and CAD-CAM mimicry compared to conventional materials [3]. Within this synthetic material class, also insight will be provided on the shape memory properties of polyester-based AUPs (two filed patents). Both chain growth and step growth polymerization mechanisms (see figure) along with their mechanical properties and processability potential will also be addressed.

Several polymer processing techniques will be covered including conventional 3D printing using the Bioscaffold 3.1 and two-photon polymerization [4,5]. A number of biomedical applications will be tackled including adipose tissue engineering [6,7], vascularization [8], ocular applications [9], etc. In a final part, attention will be paid to the valorization of our biomaterial platform technology through the launch of our spin-off company Xpect-INX. The results show that chemistry is a valuable tool to tailor the properties of (bio)polymers towards processing while preserving the material biocompatibility.



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Solid-state electrocaloric cooling, from materials to devices [1]

GS4

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The conventional vapor compression refrigeration (VCR) has high energy consumption, poor cooling efficiency and negative environmental impacts yet it is still the current and ubiquitous cooling technology. Its working principle is based on applying and removing external work to a refrigerant, which induces a phase transition with heat ejection or absorption. In this colloquium we will present an alternative solution, addressing the adverse issues of the VCR, the electrocaloric (EC) cooling. The EC cooling utilizes an electric field to induce a dipolar order-disorder phase transition where a reversible temperature change enables the heat pumping. More precisely, we are developing a ground-breaking concept of a polymer printable "solid-state" EC cooling module using static thermal switches. To enable this we: a) synthesize original nanostructured ferroelectric/relaxor-ferroelectric poly(vinylidene fluoride) (FE/RFE PVDF) polymers using chemical and physical modification methodologies introducing in controlled manner functionalities such as double bonds and photo-crosslinkable moieties to enhance the EC properties beyond the state-of-the-art, b) nanoconfine FE/RFE PVDF polymers in a heat conducting template, c) fabricate a multilayer EC capacitor, based on FE/RFE PVDF polymers, *via* printing process technologies allowing the safe operation of the EC cooling module by using low applied voltage for the phase transition all by maintaining a high efficiency derived from the EC properties. With this presentation, we will try to put forward our very recent efforts on tailor-made functional electrocaloric polymer materials associated to printable "solid-state" EC cooling modules, towards a promising alternative to VCR technology with higher efficiencies, lower environmental impact and better energy performance for which important perspectives are envisioned in the electronics, medical and food preservation sectors.

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Apatites are a class of complex and diverse materials that have gained importance because of their biological role. One of the major constituents of bone and hard tissues in mammals is a calcium phosphate whose structure closely resembles hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. This biological apatite is poorly crystallized, non-stoichiometric with multiple cationic and anionic substitutions.

Hydroxyapatite is also found in pathological calcifications. Indeed, the first steps for the formation of some kidney stones may involve deposits of nanocrystalline carbonated hydroxyapatite, commonly called Randall plaques, which are considered nucleation centers. Apatite growth can also be promoted by bioactive synthetic materials used as implants and these biomaterials play a major role in the manufacture of artificial bone material and as a coating on surgical implants.

In all these examples, the apatite phase is nanocrystalline or amorphous with a chemical composition that varies due to the ability of the structure to accommodate a large number of cationic or anionic substituents. This structural versatility allows precise adjustment of the properties in terms of bioactivity, but makes difficult the characterization of these substituted apatites.

This presentation will highlight how the use of multidimensional solid-state NMR techniques recently coupled with Dynamic Nuclear Polarization (DNP) allows for better structural characterization of synthetic or biological apatites.

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(Magneto)thermopower and thermal conductivity in oxides and sulfides

GS6

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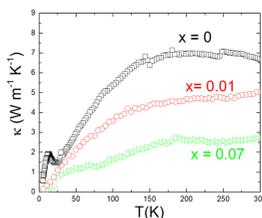
• CRISMAT - LABORATOIRE DE CRISTALLOGRAPHIE ET SCIENCES DES MATÉRIAUX
NORMANDIE UNIVERSITÉ - CNRS



According to their low toxicity and robustness against oxidizing conditions, thermoelectric ceramics of transition metal oxides or sulfides have been studied by many research teams over the world. The p-type oxides such as layered cobaltites [1,2], perovskite and hollandite ruthenates [3-5], exhibit a spin driven contribution to the thermopower which can be revealed by magnetothermopower (MTEP) measurements.

We have more recently shown for the first time that MTEP effect also exists in magnetic sulfides such as the CuCrTiS_4 spinel SPS densified ceramic [6]. These results allowed to generalize the effect of magnetism on the Seebeck coefficient (S).

This is in marked contrast with the control of the thermopower by tuning the charge carrier concentration in n-type oxides as $\text{Zn}_{1-x}\text{In}_x\text{O}$ [7] and sulfides as Fe_xTiS_2 [8]. For the latter, the chemical substitution or intercalation are efficient to reduce the lattice part of the thermal conductivity (κ) as well as to optimize the power factor (S^2/ρ , where ρ is the electrical resistivity). In that respect, the pyrites family is an interesting system as in this simple cubic structure, κ can be drastically reduced by doping such as the Cu effect in NiS_2 [9] (inset: thermal conductivity κ of $\text{Ni}_{1-x}\text{Cu}_x\text{S}_2$ ceramics; with 7%Cu only, κ is decreased by a factor of 2 at RT).



Through several examples, including tellurides such as the Sb_2Te_3 /graphite nanocomposites [10], the different routes to improve the thermoelectric properties of thermoelectric dense ceramics will be proposed.

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Electrochemistry at the nanoscale: understanding ion adsorption/transfer in electrodes for energy storage applications

GS7

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Growing demand for fast charging electrochemical energy storage devices with long cycle lifetimes for portable electronics has led to a desire for alternatives to current battery systems, which store energy *via* slow, diffusion-limited faradaic reactions. The closest devices that fit these demands are Electrochemical Double Layer Capacitors (EDLCs) which can be fully charged within minutes, with almost unlimited cyclability. The past years have shown important performance improvement in EDLCs performance thanks to the design of porous carbons and electrolytes with tailored properties. However, although EDLCs are now used in several applications including for the ever-growing electric mobility market (trams and hybrid electric vehicles), the main challenge for ECs lies in the improvement of their energy density and this is why pseudocapacitive materials are extensively investigated in the literature.

This presentation will give an overview of the research work we achieved on capacitive (porous carbon) and high-rate performance redox materials, as well as on challenges/limitations associated with their development. Starting with porous carbons, we will present the state-of-the art of the fundamental of ion transfer and adsorption in porous carbons [1-3], and will show how those discoveries have shaped the field of supercapacitors. In a second part of the talk, we will present our work on high-rate redox (pseudocapacitive) materials, with a focus on MXenes. MXenes are two-dimensional (2D) early transition metal carbides and nitrides, which are usually produced by selective etching of the A group element from MAX phases [4-6]. The careful control of the electrode architecture and surface composition have led to drastic improvement of the performance of these materials which now offers interesting perspectives to design high energy and high power energy storage devices.

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Organometallic nanoparticles for magnetically induced catalysis

GS8

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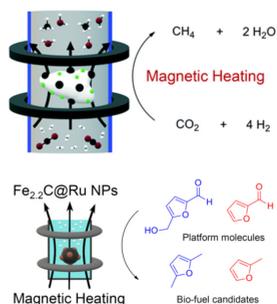
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Magnetic nanoparticles display both interesting core physical properties and interesting surface chemical properties. The composition of the particles allows to modulate their magnetic properties in terms of saturation magnetization, magnetic anisotropy and Curie temperature and hence heating power. Thus magnetic nanoparticles heat when submitted to an alternating magnetic field. Magnetic heating is instantaneous and in principle the best way to transform electrical energy into heat.

We have developed in Toulouse a new generation of iron based nanoparticles (NPs) of unprecedented heating power. We have prepared iron carbide particles by carbidization of preformed monodisperse Fe(0) nanoparticles under a CO/H₂ atmosphere at 150°C. They consist essentially of crystalline Fe_{2.2}C, display a SAR (heating power) of up to 3.3 kW/g and are able to hydrogenate CO₂ into methane in a flow reactor after addition of a catalytic Ru or Ni layer and excitation by an alternating magnetic field.[1] Iron Cobalt NPs have been prepared from {Fe[N(TMS)₂]₂}₂ and the relative {Co[N(TMS)₂]₂}₂. These soft magnetic bimetallic FeCo NPs [2] with a high Curie Temperature allow performing high temperature catalytic reactions such as propane dehydrogenation or methane and propane dry reforming. Iron nickel nanoparticles have been synthesized from iron amide and nickel amidinate precursors and found very active for CO₂ hydrogenation. In addition, submitting nanoparticles of iron carbide or iron nickel to magnetic heating in solution leads to high local over-heating and to perform in apparent mild conditions and under a low H₂ pressure difficult reactions typically performed at high temperature and pressure such as such as hydrodeoxygenation of biomass derived platform molecules.



The lecture will briefly present the synthesis of the particles, their magnetic properties, their surface modification to deposit a catalytic layer and their catalytic properties for heterogeneous CO₂ hydrogenation [1,3] in a flow reactor, dry reforming of methane [4] and in solution hydrodeoxygenation or hydrogenolysis of biomass derived platform molecules. [5,6] Further developments of the technique in solution or for water electrolysis will also be described.[7]

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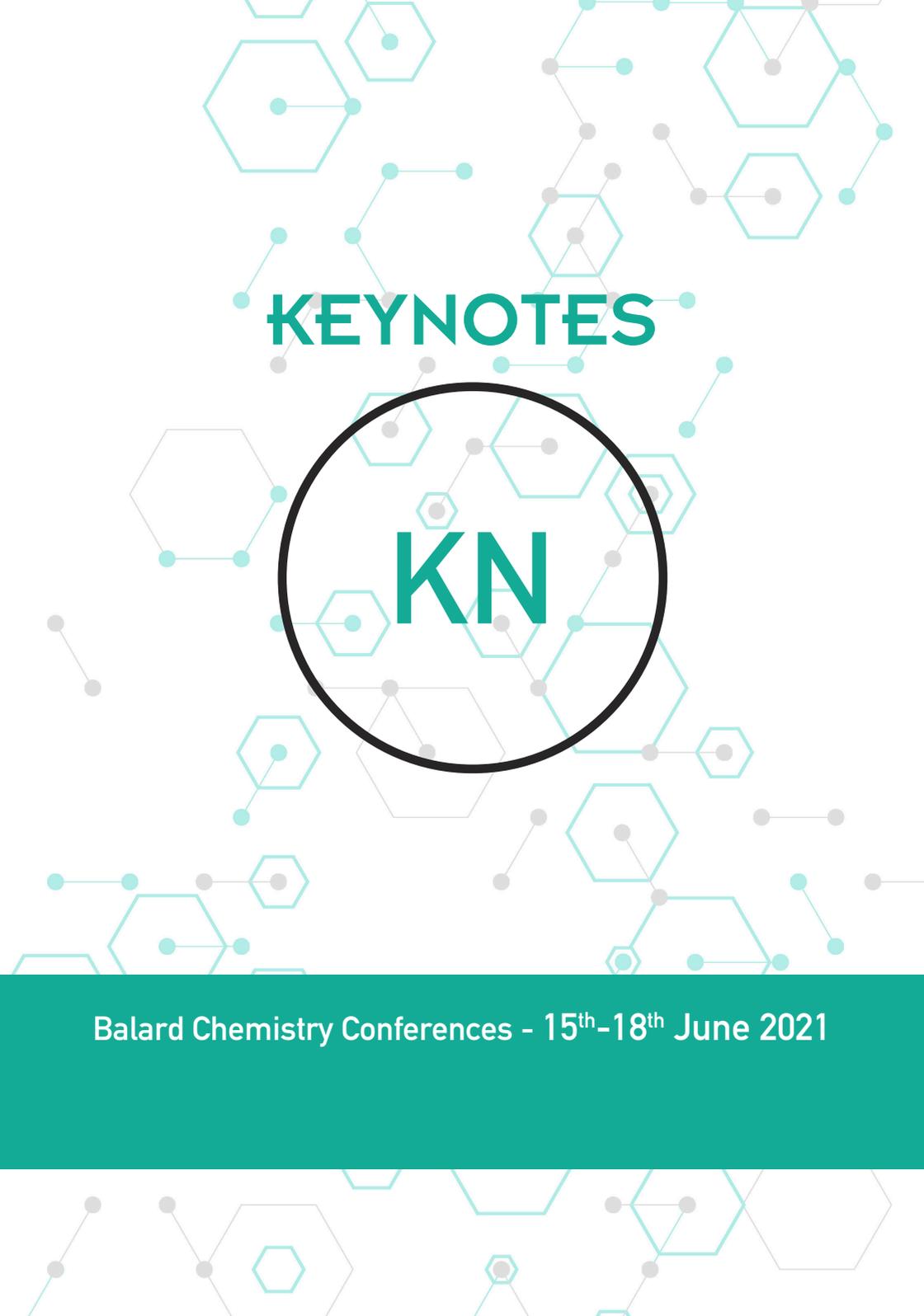
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KEYNOTES



KN

Balard Chemistry Conferences - 15th-18th June 2021

Functional 3D-nanofiber-hydrogel composites for biomedical applications

KN1

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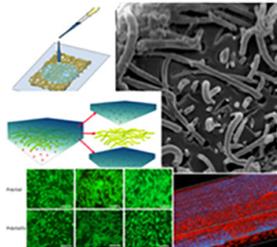
• DEPARTMENT OF CHEMISTRY "GIACOMO CIAMICIAN"
UNIVERSITY OF BOLOGNA



Bioresorbable and biocompatible 3D-nanofibrous-hydrogel composites have great potential as implantable devices for tissue regeneration and drug delivery applications. They are endowed with advantageous properties such as biodegradability, tailored mechanical properties, and the possibility to be easily modified to introduce specific functionalities. In this presentation, some examples of polymeric nanofiber-hydrogel composite devices are presented.

As a first example, a novel 3D-composite scaffold made by an RGD-mimic polyamidoamine AGMA1 hydrogel and continuous poly-L-lactide (PLLA) electrospun nanofibers will be presented. The scaffold's design was inspired by the overall structure of tissue extracellular matrix (ECM). The main idea was to combine the biomimetic properties and the hydrogel component's softness with the strength of the nanofibrous PLLA mat. Biological studies demonstrated that the scaffolds supported short-term self-renewal of Human Pluripotent Stem cells in feeder-free conditions and that the cells fully retained stemness for at least 7 days [1].

A second hydrogel-nanofiber composite scaffold, innovative in terms of structure and materials with respect to the so-far employed resorbable polymeric implants, was designed and investigated for spine interbody fusion. The scaffold is characterized by a multi-layer structure consisting of a poly(D,L-lactide-co-glycolide)/polyethylene glycol electrospun nanofibrous mat sandwiched between two hydrogel gelatin layers containing tantalum nanoparticles. The employed materials are selected



to endow the final device with biomimetic and osteoinductive properties. The *in vitro* tests demonstrate that the obtained scaffolds represent a favorable milieu for normal human bone-marrow-derived mesenchymal stem cell viability and osteoblastic differentiation; moreover, the inclusion of tantalum nanoparticles in the scaffold improves cell performance with particular regard to early and late markers of osteoblastic differentiation.

The nanofiber-hydrogel composite material can also be used as an implantable scaffold for multi-drug release. In-situ release of multiple drugs in a controlled way has been a hot topic during the last decades. A novel dual drug delivery biodegradable composite was designed to obtain a fast release of an anticancer drug, such as epirubicin or chlortetracycline hydrochloride (CTC, a model anticancer drug), and a sustained release of diclofenac (DK) as an anti-inflammatory drug. The possibility to tune the drug release by tailoring the architecture and chemical composition of the final composites was demonstrated. These composites might find applications as in-situ patches to be applied after a surgical intervention such as surgical tumor resection, preventing relapse, and promoting patient's recovery.

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Artificial water channels-toward biomimetic membranes for desalination

KN2

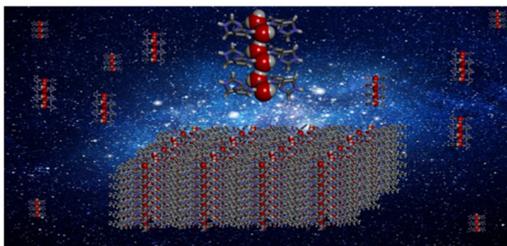
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This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful to understanding many biological scenarios. Moreover, they can be used for the preparation of highly selective membranes for desalination.



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Zeolite as a major solution for molecular decontamination in space

KN3

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Space industries are really concerned by a major issue: molecular contamination. Indeed, once satellites are in orbit, molecules contained in paints, adhesives or glues can outgas and form films or droplets on the surface of mirrors, lenses, solar cells or thermal detectors. The National Aeronautic and Space Administration (NASA) and the French Space Agency (CNES) have investigated the chemical nature of these molecules; hydrocarbons and plasticizers were identified as the most important part of the outgassed molecules.[1] Those molecules can deposit on the surface of on-boarded equipment like optics and damage them. After testing several porous materials as molecular adsorbents to fix the molecular contamination issue, zeolites have been designed as the ideal candidates thanks to their great adsorption capacities, and especially their ability to trap the volatile organic compounds at very low concentration in the atmosphere. Synthetic zeolites are generally obtained as powders leading to non-bonded particles. In space application, zeolite have to be shaped to avoid particulate contamination. Nonetheless, it is necessary to introduce additives to increase the mechanical properties of the shaped zeolites. Usually, very large amounts of binders, such as clays, silica based compounds or aluminum base compounds are used to link zeolite crystals together in order to produce bodies with high mechanical resistance and optimal dimensions. Hence, methods that allow the shaping of zeolite powder with a small amount of binder and a high mechanical resistance are highly desired.

We have shown in collaboration with the French Space Agency (CNES) that zeolites could be successfully used to adsorb volatile organic compounds in satellites [2-6] once they are shaped (films, pellets, beads, painting, etc). A zeolite pellet elaborated in Mulhouse is used for trapping pollutants within the ChemCam instrument on-board the Curiosity Robot currently on Mars (see Figure 1).

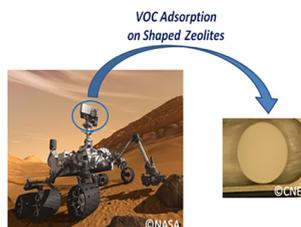


Figure 1: Zeolite Pellet in the head of the Curiosity Robot.

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Modelling of MOF/polymer composites: from compatibility to performance

KN4

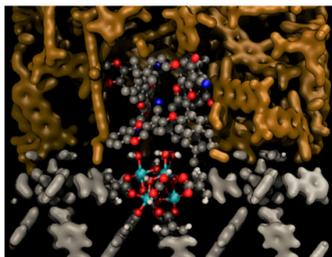
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Metal-Organic Framework/Polymer Mixed Matrix Membranes (MMMs) have attracted great interest in the past few years as a promising alternative to the polymer membranes currently used for gas separation processes. [1] Although many experimental studies have focused on the elaboration and efficacy of such MMMs for specific gas separations, increasing our fundamental understanding on both the interfacial structure of these composites and the molecular mechanism of the separation phenomena is still necessary for devising optimization strategies for their industrial applications. In this keynote lecture I will present an overview of our recent advances in understanding MOF/polymer compatibility and gas separation performances *via* computer simulations. I will introduce the different computational methodologies that were developed, including all-atom [2] and coarse-graining [3] models integrated into equilibrium and non-equilibrium molecular dynamics and Monte Carlo schemes.[4,5] and how they have allowed us to identify the microscopic parameters that govern MOF/polymer affinity,[6] and whether this affinity is related to the performance of the composite as an adsorbent.[7] Finally, I will detail the challenges that we still need to tackle in order to aspire to a rational design of MOF/polymer composites for target applications.



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Design of porous composites by assembling MOFs with (bio)macromolecules or carbon based materials for environmental related applications.

KN5

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Nanocomposites offer unique advantage to enable integration, miniaturisation and multi-functionalisation of devices. In the past few years, significant research interest was devoted to Metal–Organic Frameworks (MOFs) due to the precise and remarkable design of their framework and porosity at the molecular length scale. MOFs are thus considered as an intriguing class of porous materials with a high potential for numerous applications including gas storage/separation, catalysis, sensing, electronics, biomedicine etc... The assembling of MOFs with a variety of organic components and functional nanoparticles was envisaged not only to process MOFs and enhance their stability but also to impart synergistic functionalities.

Here we present our progress in the development of MOFs based composites to address environmental and energy-related applications. Due to their outstanding gas and liquid separation properties, MOF nanoparticles were incorporated as selective porous fillers in polymer matrices to form mixed matrix membranes. These composite membranes combine the attractive transport and separation properties of the incorporated MOFs nanoparticles with the good processability and mechanical properties of the polymers. We have explored different strategies to process MOF-polymer mixed matrix membranes for the capture of small gas molecules (i. e. CO₂).^[1,2] Since the transport properties of the membranes result from a strong interplay between their morphology, thickness, microstructure and the balance between hydrophilic/hydrophobic regions, we have optimized the morphology/diameter and surface functionalization of MOFs nanoparticles for their integration in the polymer matrix. Recently, it was shown that MOFs could be of interest for the selective capture of volatile organic compounds (VOCs) in the presence of moisture, especially the harmful acetic acid generated by the degradation of cellulose based cultural artifacts.^[3] We have thus combined MOFs with biopolymers to process selective adsorbents of acetic acid in humid conditions for cultural heritage preservation. The last part of this presentation will be devoted to core-shell MOF-graphene oxide (GO) composites.^[4] Here we have taken profit of the self-organization properties of GO to tune the organization and nanostructuring of composites as well as control the morphology of MOF nanocrystals. We have combined advanced characterization tools (TEM analytical/imaging techniques and electron diffraction) to provide a complete picture of these composites at the nanoscale and describe their interfacial properties.

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Porous silicon, a biodegradable semiconductor for nanomedicine

KN6

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The application of nanotechnologies into medicine promises to offer solutions when applied to health challenges such as cancer. Our research projects aim to develop biodegradable multifunctional anti-cancer materials based on mesoporous silicon-based nanostructures to be used for the local treatment of cancer. Porous silicon nanoparticles (pSiNP) are fully bioresorbable, and nontoxic *in vivo*, in addition they can be excited by near infrared (NIR) two photon excitation light offering possibilities for phototherapies, and for light triggered and focalized treatment.

The development of photoactive porous silicon nanovectors functionalized with organic ligands for applications in imaging, nucleic acids and drug delivery, as well as photo-activated therapies will be presented [1-5].

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Conceptual architectonic of luminescent nanoparticles for optical imaging and temperature sensing

KN7

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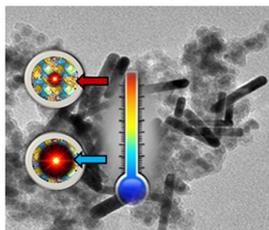
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Luminescent nanoparticles have gained particular attention these last years since many applications of such materials in structural and functional *in vivo* imaging (early diagnosis of tumors, cell's biodistribution) as well as in the development of new devices for the energy transition (photovoltaic, LED lighting and display). Among the possible applications, bioimaging has been successfully established with persistent luminescent nanoparticles which emit in the region of partial transparency of living tissues in the red/near infrared range. Their use has a clear advantage as the irradiation step to create optical excited states, can be performed before injection, avoiding tissue stress and other autofluorescence phenomena [1]. Luminescent particles are also used as local optical temperature probes in the nanoscale. The emergence of luminescence nanothermometry is based on the very strong dependence of radiative phenomena on temperature and the remarkable sensitivity of luminescent probes.

Here, we will present synthesis strategies used for the creation of architected luminescent nanoparticles allowing to adjust luminescent parameters, namely, intensity, spectral position, lifetime, brightness, thermal sensitivity and stability. We will develop recent advances on thermosensitive probe emitting in the first and second NIR windows and that are relevant to perform in real-time local temperature readings. We will demonstrate that such optical nanoprobe has now reached sufficient maturity to focus on the demonstration of nanothermometry applications and the expected benefits of nanothermometry for safer biological hyperthermia treatment and for the development of sustainable catalysis.



We will focus on small ZnGa_2O_4 doped with chromium (NIR-I) obtained by hydrothermal synthesis assisted by microwave heating for purposes of illustration. The mechanism of the persistent luminescence properties of this material will be discussed regarding dopant local environment. As the luminescence lifetime of the 2E emitted state is drastically dependent on temperature since the $^4\text{T}_2$ and ^2E levels are in thermal equilibrium, ZnGa_2O_4 is then used as thermal nanosensor for temperature measurement of plasmonic gold nanorods [3]. Preliminary results on nanothermometry for magnetic hyperthermia application using Ag_2S as quantum dots emitting in NIR-II will be finally presented.

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Shuffling alkali ions in layered transitions metal oxides: crystallochemistry, challenges and possible applications

KN8

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The family of layered alkali transition metal oxides AMO_2 gather a wide range of chemical compositions and various correlated physical properties. These crystalline oxides exhibit a layered structure with a stacking of edge-shared MO_6 octahedra sheets, with alkali ions sandwiched in-between.

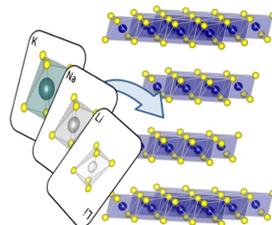
Such particular crystallographic structure represents a perfect platform for reversible electrochemical removal. Consequently, these compounds are logically investigated as electrode materials for rechargeable metal-ion batteries.

Cationic substitutions within the transition metal layers are easy to achieve and this chemical diversity offers a wonderful playground for chemists and physicists to design multi-metal layered oxides and tune their properties. Here, we will focus on alkali-mixed compositions. Indeed, there are surprisingly very few examples of compounds combining two different alkali ions inside their layered structure.

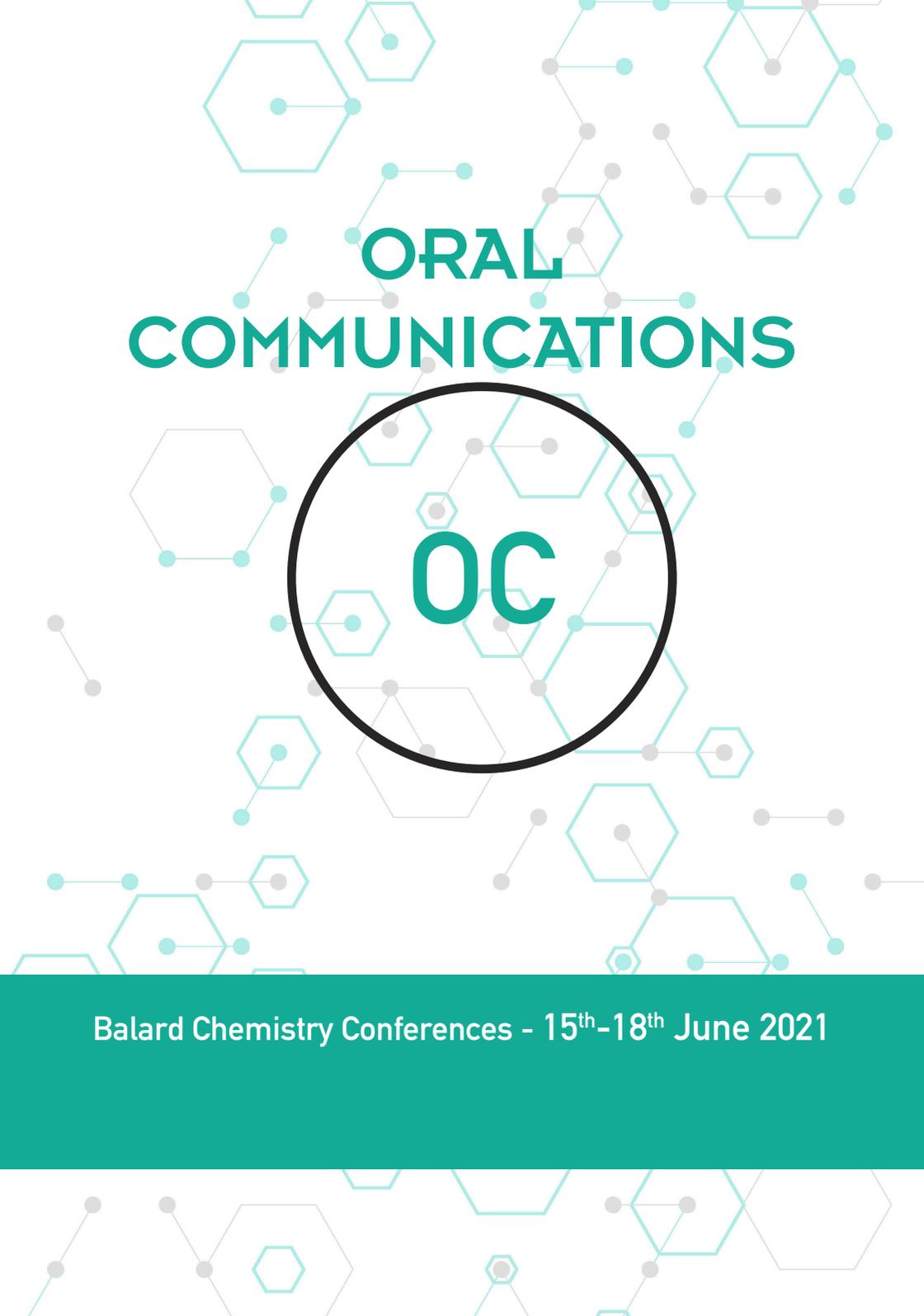
In the first part of this presentation, the crystallographic organization of alkali transition metal oxides will be described, with a particular focus the different stacking that are available following the site symmetry of the alkali ion and how these compounds are characterized by X-ray diffraction and solid-state nuclear magnetic resonance spectroscopy.

Then, two systems currently investigated at ICGM will be presented: $(Li,Na)_3Ni_2SbO_6$ and $(Na,K)Ni_2TeO_6$. On top of the layered stacking, they both exhibit an additional cationic ordering with an in-plane honeycomb array Ni/Sb or Ni/Te. Whereas lithium and sodium ions occupy the same layer in $(Li,Na)_3Ni_2SbO_6$, After describing the synthesis of these compounds, we will take focus on the understanding of crystallographic structure, thanks to a combination of two characterization techniques (X-ray diffraction and solid-state nuclear magnetic resonance spectroscopy) with a theoretical approach (density functional theory calculation and stacking faults simulations).

Finally, we will discuss on the possible interest of such alkali-mixed compositions, especially by transferring this concept of the layered sulfides with exhibit an analog crystallographic structure.







ORAL COMMUNICATIONS



OC

Balard Chemistry Conferences - 15th-18th June 2021

Design of hybrid peptide / polymer nanofibers for soft tissues regeneration

OC1

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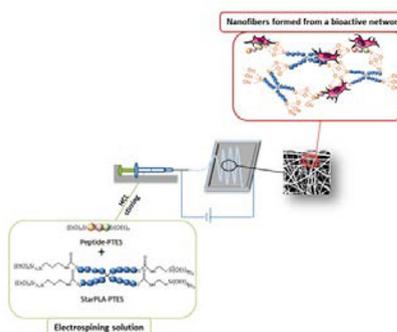
Nanofibers are excellent biomimetic supports for tissue regeneration since they mimic the architecture of the natural extracellular matrix and provide topographic characteristics necessary to modulate the fate of cells. This work aims to create new implantable and degradable nanofibers composed of PLAs functionalized with bioactive peptides to mimic the physical and biochemical properties of native matrix fibrils for tissue regeneration.

First, we synthesized and characterized star-shaped PLAs functionalized with IPTES (StarPLA-PTES) and bifunctional silylated peptides intended to react together *via* sol-gel process to create a bioactive network.

Subsequently, we produced functional nanofibers by activating the sol-gel reaction during the electrospinning process. We studied the impact of different parameters such as content of IPTES groups and amount of HCL in electrospinning solution on 1/ the formation of the three-dimensional network of polymers composing the nanofibers and 2/ the rate of incorporation of the peptide in this network.

During the fabrication of the nanofibers, we observed that the molecular weight of the polymer and the hydrolysis kinetics of the PTES functions had the most significant impact on the cross-linking of the polymer-peptide network. Interestingly, we noticed that the grafting rate of the peptides was improved with the use of low molecular weight polymers because these polymers have a high content of crosslinking groups (PTES).

In conclusion, we developed a new process to obtain nanofibers composed of a hybrid three-dimensional network containing degradable polymers covalently bonded with bioactive peptides. Both the polymers and the peptides can be modified to adapt to different disease targets. The continuation of this project will consist in evaluating the biological properties of hybrid nanofibers on skin fibroblasts.



Covalent functionalized MoS₂ membranes with tunable layer spacing for molecular sieving

OC2

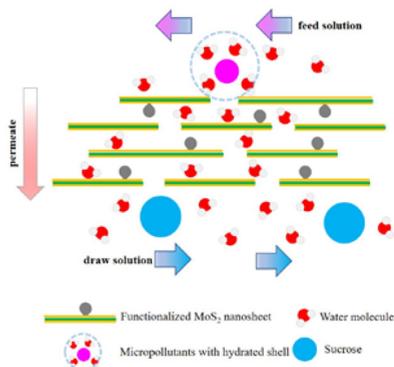
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Two-dimensional (2D) laminated membranes consisting in stacked by 2D nanosheets have shown superior molecular permeation properties, with bright prospect for separation application [1-3]. Besides the permeability, a considerable rejection is also critical when they are used for separation operation, liking water purification and ionic sieving. The high rejection can be achieved if the interlayer space (d-space) of the laminates is smaller than the diameters of hydrated ions and micropollutant molecules, which are close to sub-nanometers. Most of 2D membranes, however, tend to swell in water translating into poor stability and modest rejection performance. Therefore, achieving long-term stable laminates with sub-nano interlayer space for aqueous phase separation remains a challenge. Here, we report non-swelling and d-space tuned molybdenum disulfide (MoS₂) membranes. The interlayer channels are tunable from 3.5 to 7.7 Å using small functional groups grafted on MoS₂ nanosheets *via* covalent surface modification strategy. Those membranes exhibited remarkable separation performances in forward osmosis operation compared to those of pristine non-functionalized membranes. In my presentation, I will present our results on the d-space and the surface chemistry of the laminated membranes on the one hand and the performance of water transport, ionic permeation and molecular sieving on the other hand.



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Hybrid polymer biomaterial for tissue engineering scaffold using stereolithography

OC3

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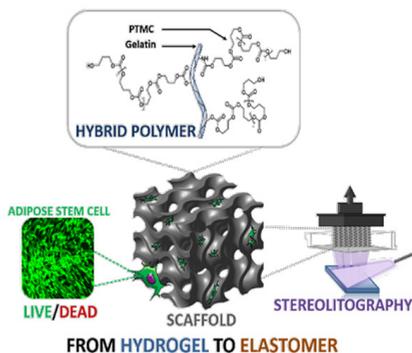
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Introduction:

Tissue engineering is widely recognized to be the most promising approach to restore, maintain, or improve tissue function. Tissue engineering scaffold fabrication remains a crucial step of this strategy. Scaffold properties and architectures are central for successful regeneration of tissue and organs. Indeed, suitable tissue engineering requires accurate microarchitectures and sophisticated scaffolding structures able to mimic the intricate architecture and complexity of the native organs and tissues. The emergence of additive manufacturing technologies offers an opportunity to design such sophisticated 3D structures. Among all the technologies, stereolithography[1] is the best approach for biomedical applications and especially in tissue engineering. Stereolithography can generate complex geometries with high resolution and quickness. From these perspectives, some resins based on gelatin have already been reported to provide favorable cellular adhesion because of the similar properties with the body tissue[2]. However, gelatin material displays ineffective mechanical properties. To that end, we investigated a new hybrid polymer based on gelatin (for its biological properties) and poly(trimethylene carbonate) (PTMC) (for its mechanical properties) and build high sophisticated scaffold by stereolithography to overcome the tissue regeneration challenge.



Experimental methods:

Polymers were synthesized by increasing grafted PTMC on gelatin ratio (from 0.2 to 20 eq. of TMC) to evaluate the impact on the mechanical and biological properties. The materials were functionalized to lead to photosensitive resins, which then have been used to build porous scaffolds by stereolithography. *In vitro* cytocompatibility and cellular adhesion/proliferation within the built scaffolds have been performed with adipose stem cell. Mechanical resistance has been evaluated by tensile and compression testing on photo-crosslinked films.

Results and discussions:

We successfully demonstrated the grafting of PTMC on the gelatin and the resulting polymeric materials were fully characterized. The different synthetic pathways allow to tune polyvalent materials from hydrogel to elastomer only by adjusting the composition of gelatin and PTMC. We determined that by increasing the PTMC on the gelatin ratio, the resistance and elongation of the material have been significantly improved. The built scaffold by stereolithography showed no cytotoxicity and remarkable cell adhesion and proliferation. This work shows the great potential of these polymers to prepare scaffold and the excellent cell behavior remains promising to restore the tissue function.

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Graphene oxide (Go) assisted polymeric hollow fibers membranes for water purification

OC4

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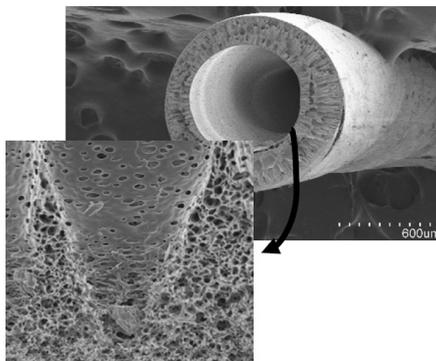
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During the past few years, fast industries development and population growth have strongly threatened the ecological environment and human health. As surface and underground water have been more and more contaminated, availability and safety of drinking water became an on-going global challenge. So far, a lot of water purification processes have been developed. Indeed, thanks to their many advantages such as high separation efficiency, easy operation, low energy consumption and their environmentally friendly behaviour [1], membranes are among the most advanced ones. Today, the leading choice for these membranes fabrication is the use of

polymer macromolecules like polysulfone (PSU) or polyvinylidene fluoride (PVDF). However, it is well known that the efficiency of membranes is directly related to the properties of their components. Indeed, the main drawback of these polymeric materials is their intrinsic hydrophobicity that affects especially antifouling performances [2]; therefore, several strategies are studied to counteract this problematic. One solution would be to add nanoscale materials with great assets like graphene oxide (GO), an atomic-layer thick nanosheet 2D material that has lately attracted interest [3] because of its exceptionally high crystal and electronic quality. Moreover, that's its noteworthy hydrophilicity due to its oxygen-rich functional groups [1,4] that has been explored for water treatment application. In fact, graphene-based membranes have already shown notably improved performances: permeability, mechanical and antifouling properties for instance [1].

This study relies on this idea. GO is added into casting solution for PSU hollow fibers membranes preparation. Different GO percentages are tested and their influence on the fibers properties is investigated. The physico-chemical properties of the membranes are determined by means of several techniques, such as Scanning Electron Microscopy (SEM), Raman, Energy Dispersive X-Ray Analysis (EDX), ThermoGravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), etc... The influence of the solution viscosity on the membrane behavior and mechanical properties using tensile tests is studied as well. Finally, the performances of the membrane in terms of water permeability, antifouling using Bovine Serum Albumin proteins (BSA), molecular cut-off threshold using PolyEthylene Glycol (PEG) molecules are investigated. Furthermore, the comparison between raw and GO modified PSU hollow fibers membranes behavior is performed.



This project is part of INNOMEM and receives funding from the European

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Liquid porous nanomaterials for liquid-liquid extraction

OC5

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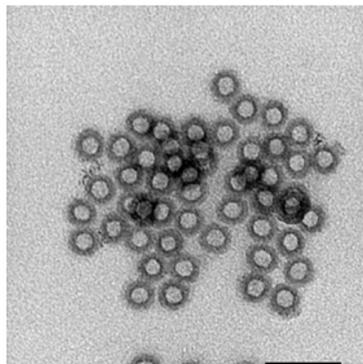
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Nowadays, separation of chemical elements is an important stake for applications as broad as ore mining, metal recycling or pharmaceutical industry. Although liquid-liquid extraction represents the most applied method at industrial scale, it involves many economic and environmental constraints related to the use of large quantities of solvents. There is therefore a growing interest for alternatives as solid-liquid separation and flotation processes, which however, would require re-designing the actual industrial installations. These alternatives present moreover limited performances, in terms of extraction and selectivity capacities. This project proposes to evaluate a new approach by replacing the organic phases of liquid-liquid extraction processes, with a porous liquid. The Oak Ridge Corporation proposed in 2014 [1], a new class of porous liquid, based on hollow silica nanospheres (HS) obtained by a surfactant templated silica sol-gel. In this work, we evaluate the application of such liquid empty cavities to extract metals from an aqueous phase. This extraction approach would be at the exact junction between the conventional liquid-liquid and solid-liquid extraction processes, taking the advantages of the two processes.

To form the porous liquid, HS were prepared thanks to the self-assembly of a surfactant in presence of oil and silica precursors. After the synthesis, the surfactant is removed by calcination and monodisperse HS are made. Various synthesis parameters were investigated to control and understand the morphology of the HS. Indeed, the size of the core, the shape and the homogeneity of the particles could be changed and controlled. TEM micrograph and SAXS data showed that we obtain highly monodisperse HS with a core radius of 6nm and silica shell of 7nm.



The HS are further grafted with an organosilane and a PEG interacting thanks to an ionic bond. This ionic corona has the property to turn the solid nanospheres into a liquid material (figure: TEM micrograph of porous liquid, scale bar 100nm).

For extraction application, it appears essential to characterize in details the structure and the permeability of these HS, not only to metallic species but in the first place, to aqueous solutions and gaz.

In order to optimize the synthesis route for enhanced permeability, adsorption of argon and nitrogen were carried out with the solid and the liquid to highlight the accessibility to gas of the porosity throughout all the steps of grafting. Gaz sorption reveals that the porosity is becoming less accessible after the grafting step, which means when the solid becomes liquid.

An adsorption study was also conducted with liquid solutions by matching the contrast of various solvent and silica by SAXS and SANS to rely the permeability and the pores structure. The SANS signal of the non-grafted HS was extinguished with a H_2O/D_2O ratio matching the scattering length density of nanosphere's silica. It allowed us understanding the permeability of reference HS to solvent, specifically if and how the grafting influences the solvent permeability.

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Optimizing intact protein separation using capillary electrophoresis

OC6

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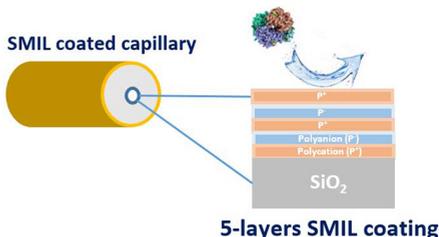


Capillary electrophoresis (CE) is an analytical technique that is increasingly used to separate proteins, notably for therapeutic applications, thanks to its selectivity, efficiency and its coupling with mass spectrometry. In theory, separation is controlled by axial diffusion and a million theoretical plates should be reached. In practice, separation efficiency is limited by the adsorption of proteins onto the inner capillary wall. To limit this phenomenon, capillary coatings made of successive multi-ionic polymer layers (SMIL) can be used, alternating polycations and polyanions in order to increase the distance between proteins and the capillary wall. The quality of the coating depends on polyelectrolyte nature, separation buffer nature and pH, the number of layers [1] and the preparation of the protein sample to be analyzed.

Comparing separation efficiencies for different SMIL coatings is delicate, since electroosmotic flows and analysis times vary from one coating to another. However, protein adsorption onto the capillary wall may be quantified by determining the retention factor k , which is calculated by repeating separations at different electric fields. Despite low values of k , between 0.01 and 0.1, residual adsorption has a notable impact on separation efficiency in CE [2]. It is therefore crucial to reduce the residual adsorption by optimizing the capillary coatings.

In this work, retention factors obtained for the separation of intact model proteins (trypsin inhibitor, myoglobin, ribonuclease A and lysozyme) in acetic acid (2M) using different polyelectrolyte multilayer capillary coatings were compared. As a first step, heating the protein sample prepared in the analysis buffer was shown to improve repeatability in the separation efficiency. Next, the use of a ramified polyethyleneimine (PEI), known to enhance surface homogeneity in other applications [3], was incorporated in the coating as the first layer. The influence of the number of polyelectrolyte layers on SMIL robustness and k values were investigated. To this end, different polycation (poly(diallyldimethylammonium) chloride (PDADMAC), polybrene (PB), and quaternized diethylaminoethyl dextran (DEAEDq)) and polyanion (poly(styrene sulfonate) (PSS) and poly(methacrylic acid) (PMA)) couples were tested. A ranking of capillary coatings was therefore achieved with significantly improved protein separation efficiencies.

This work was realized within the scope of a PRCI in collaboration with German partners from the University of Aalen, Germany (ANR-DFG SMILE).



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Synergetic self-assembly of alkylureido systems into artificial water channels

OC7

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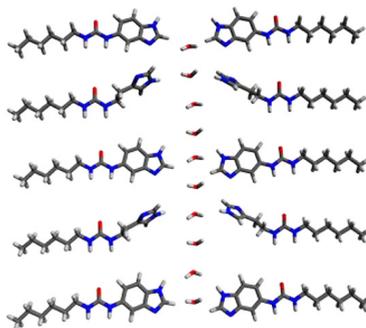


Water translocation through cell membranes plays an important role for living organisms. In cells, the transport of water molecules is carried out through water-transporting proteins, namely aquaporins [1]. Promising artificial water channels (AWCs) are Imidazole-quartet systems in which the channels within 2.6-Å pores formed from the supramolecular organization of alkylureido-ethylimidazole compounds. Values of pore diameter, water permeability and ion rejection of these AWCs are on par with very efficient aquaporins [2, 3]. Whilst the size restriction is still one of the main criteria for AWC, the specific water recognition is necessary

for selectivity. The selective binding of water can be obtained through the synergetic combination of donor-acceptor H-bonding components, while the permeability is determined by the friction-less translocation.

This work describes novel alkylureido-AWCs and their bi-component optimal self-assembly that induce the selective transport of water against the ions. A series of ureido derivatives were prepared by reacting aromatic amines containing donor and/or acceptor H-bonding fragments with alkyl isocyanates. The obtained derivatives and their combinations were evaluated in terms of water and ion transport activities by using stopped-flow method and fluorescent HPTS assay, respectively. It

is marked that water permeability for some bi-component systems are multiply times higher compared to single compound without significant ion transport both for single compounds and their combinations. Thus, the net permeability for system of hexylureido-ethylimidazole and hexylureido-1H-benzo[d]imidazole (HC6/S5-6, molar ratio is 1:1) is $22 \mu\text{m}\cdot\text{s}^{-1}$; for single compounds are $2 \mu\text{m}\cdot\text{s}^{-1}$ and $10 \mu\text{m}\cdot\text{s}^{-1}$, respectively, which is indicating that a synergetic self-assembly of two compounds into bi-component AWC occurs. Single channel permeability of HC6/S5-6 system was increased 5 times compared to imidazole-quartet systems formed by self-assembly of HC6 ($5.22\cdot 10^7$ water molecules/s/channel for HC6/S5-6 system and $1.09\cdot 10^7$ water molecules/s/channel for HC6), which is only 2 order of magnitude less than aquaporin ($4\cdot 10^9$ water molecules/s/channel).



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Design of degradable elastomers and hydrogels for the conception of bioresorbable anti-inflammatory patches

OC8

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Degradable elastomers and hydrogels are largely spread among biomedical applications owing to their potentials for use in medical devices, like surgical patches, or as drug delivery systems, like subcutaneous therapeutic depot [1,2]. However, standard linear elastomers prepolymers present some limitations: difficulty to modulate and reach the adequate properties due to their low molecular weight, limited functionality leading to low crosslinking efficiencies if no toxic photoinitiators are used.

To overcome these limitations, our team recently designed eight-armed polyether-polyester star block copolymers, composed of eight-arm poly(ethylene glycol) core and poly(lactide) or poly(caprolactone) side arms. These copolymers exhibited a significant interest, since it is possible to obtain either elastomer or hydrogel by adjusting the polyether-polyester ratio[3,4]. Moreover, once the polymers have been synthesized by ring opening polymerization, the chain ends can be functionalized either with (meth) acrylic groups to allow UV cross-linking or with bioadhesive groups to promote bioadhesion.

These copolymers are currently developed to produce a biodegradable self-rolled/self-unrolled multi-layer patch that could be applied locally by colonoscopy without surgical intervention to treat alterations of colonic tissue induced by radiotherapy.

This patch will act as a dressing loaded with anti-inflammatory molecules that could protect and heal the ulcerated zone. One major objective is to design the patch so that i) it facilitates the placement into the colon by surgeons under a rolled shape and ii) it then self-unrolls and adheres to the ulcerated zone to permit a targeted unidirectional release toward tissues.

In this communication, we will present the methodology to build this patch. In more details, we will detail the synthesis of the polymers and the preparation of the elastomeric/hydrogel bi-layered construct and its cross-linking under UV irradiation. Various combination of degradable elastomers and hydrogels will be investigated. The mechanical properties of each layer and of the patch will be discussed. The similar nature of the two layers is expected to enhance their cohesion. Finally, evaluation of the patch ability to self-rolling [5] due to the different swelling behaviours of the two layers and its loading capacities with drugs will be presented.

Multi-layer structure model



Self-rolled patch prototype



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Carbon aerogels as catalysts supports for hydrogenation reactions of organic molecules

OC9

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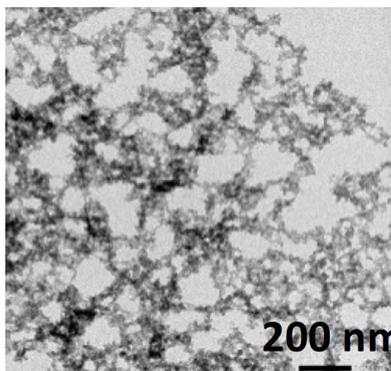
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Hydrothermal carbonization of molecules from biomass allows to obtain carbon porous materials under relatively mild conditions of temperature and pressure (180°C, $p < 10$ bars) [1]. The aim of this work is to synthesize carbon materials with controlled hierarchical porosity (micro, meso and macroporosity) through solvothermal carbonization of monosaccharides (e.g. fructose, xylose) and phenolic components (e.g. phloroglucinol, tannin) [2]. In particular, both microporous and macroporous carbon aerogels are obtained by lyophilisation of gels followed by pyrolysis. These aerogels (or cryogels) show high specific surfaces and porous volumes, in the order of $800 \text{ m}^2 \cdot \text{g}^{-1}$ and $2 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively (figure).

These aerogels are used as supports for metallic nanoparticles (e.g. Pt, Ru, Ni, Co). In order to realise, two approaches are developed: (i) dry impregnation of previously synthesized aerogels; and (ii) one-pot synthesis which allows the formation of metallic nanoparticles jointly by the solvothermal carbonization of organic precursors. The latter approach is original and allows the homogeneously incorporation of metallic particles of few nanometres in the carbon skeleton. The obtained aerogels type C/Metal are used as catalysts for selective hydrogenation reactions of organic molecules (i.e., 4-chloronitrobenzene and levulinic acid) and compared with commercial catalysts [3].



The metal (size of particles, concentration, dispersion on the support) as well as the support (texture, specific surface) are key parameters in the control of hydrogenation selectivity. In addition, electrocatalytic properties of these carbon aerogels are likewise investigated for electrochemical hydrogenation reactions which have the advantage to take place under ambient temperature and atmospheric pressure without the need of molecular hydrogen.

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Selective laser sintering of solid oral dosage forms with Copovidone and Paracetamol using a CO₂ laser

OC10

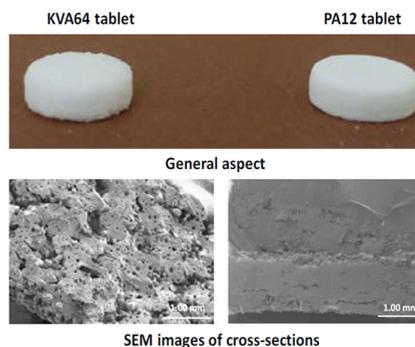
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Material suitability is a necessary aspect to take in consideration for the design of pharmaceutical solid oral forms. With the advent of new pharmaceutical production processes like additive manufacturing, critical quality attributes of raw materials need to be rethought. Previous studies revealed that 3D-printing of solid oral forms (SOFs) by selective laser sintering (SLS) requires the addition of an absorbance enhancer since none of the used polymers including copovidone absorb at the used laser's wavelength ($\lambda = 445 \mu\text{m}$)[1]. The aim of this work is to assess the suitability of a CO₂ laser ($\lambda = 10.6 \mu\text{m}$) for selective laser sintering of SOFs containing copovidone and paracetamol. Prior to printing, physicochemical characterization (study of flowability and compactness, infrared absorbance) was conducted on the different powders (two different grades of copovidone, two grades of paracetamol, mixtures of the two grades of copovidone at different proportions, and formulations of copovidone and paracetamol at various ratios), to determine the relationship between the properties of materials and their printability. Polyamide 12 was taken as a reference material to interpret the results of powder characterization. Then, the properties of the printed SOFs were evaluated (porosity, hardness, drug content and release). Results evidenced that copovidone absorbs the infrared light at the laser's wavelength region, which resulted in the ability of the polymer to sinter without the use of an absorbance enhancer. It was found that a fair flow was a necessary condition to achieve printing by allowing the formation of a flat layer. The lower compactness of copovidone and the different mixtures compared to polyamide 12, reduced the mechanical properties of the SOFs but also increased their porosity, which can be exploited to modulate drug release. Moreover, the drug did not undergo degradation despite the high energy of the CO₂ laser, and demonstrated a plasticizer effect by lowering the heating temperature during printing. Moreover, the paper defines some pre-screening tools that should be employed to choose suitable materials for the production of SOFs by SLS: evaluation of the absorbance at the laser's wavelength using FTIR, measurement of bulk density to appreciate powder compactness and study of flowability by calculation of Hausner ratio and angle of repose. In conclusion, this work proves the applicability of CO₂ laser SLS printer to produce SOFs.



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Low-temperature selective catalytic reduction of NO by NH₃ over HKUST-1 catalysts impregnated with Mn

OC11

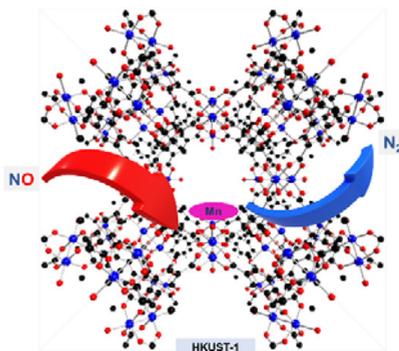
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Air quality preservation is undoubtedly one of the major environmental issues facing our society. The reduction of nitrogen oxides (NO_x) emissions is demanded due to the photochemical smog, ozone depletion, and acid rains. Selective catalytic reduction of nitrogen oxides by NH₃ (NH₃-SCR) is a well-known process with an efficient approach for removing air-polluting NO_x. At present, for stationary sources, the most commonly applied catalyst is V₂O₅-WO₃(MoO₃)/TiO₂ (vanadium plays the role of active phase). This material allows high conversion of NO_x, however, its application is limited by relatively narrow and high-temperature window (300–400°C) and toxicity of vanadium oxide.[1] Therefore, finding a novel eco-friendly material with high NH₃-SCR activity at temperatures lower than 250°C is a big challenge. Up to now, fruitful research has been made on the alternative supported catalysts containing Mn, being active and stable in the NH₃-SCR.[2] Modified Metal-Organic Frameworks (MOFs) are one of the promising candidates for NH₃-SCR. MOFs are crystalline hybrid porous solids, built from organic linkers and inorganic nodes.[3] Their enhanced specific surface area, porosity, and tunable topologies have already attracted much attention in catalysis.[3–5] Copper-containing materials are a great alternative for NO_x removal, since Cu is an essential redox center for the NH₃-SCR reaction.[6]



We choose to explore the potential of HKUST-1, a MOF based on copper paddle-wheel and benzene-1,3,5-tricarboxylate (Cu-BTC) with the high specific surface area for NH₃-SCR of NO_x. Only a few studies are available on MOF as catalysts for NH₃-SCR and they report some activity at low temperature through the presentation of NO_x conversion only.[4,5]

In our work, we focused on facile modification of HKUST-1 with different loadings of Mn (2.5, 3.75, 5.0, 7.5, and 10 wt.%). The modification with 2.5 and 5.0 wt.% of Mn was recognized to be beneficial as it resulted in the creation of new mesopores, allowing molecules to access the framework of MOF. On the other hand, the addition of higher Mn content (7.5 and 10 wt.%) led to a partial destruction of the HKUST-1 crystals and the formation of wider pores, accompanied by a significant decrease of the microporous volume. The efficiency in NO reduction with NH₃ measured at 185°C increased with the manganese content up to 3.75 wt.% and then decreased. For HKUST-1-Mn3.75 catalyst, 68% of NO conversion was reached at 185°C (WHSV=96,000 ml/h-g). The H₂O and SO₂ tolerance was examined.

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Alloys negative electrode for Mg-ion/S batteries

OC12

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Lithium-ion batteries have revolutionized the field of energy storage. World battery production has exploded in recent years, and the demand will continue to grow in the future. However, there are fears of supply or cost problems for certain raw materials (cobalt and nickel used in the composition of positive electrode materials). Faced with this observation, it is therefore important to consider an alternatives to lithium-ion technology.

Among the so-called "post-lithium" systems, the Mg-ion batteries are interesting. Magnesium theoretically have high capacity and low redox potential that is compatible with the design of batteries with high energy densities. However, the difficult diffusion of divalent ions (Mg^{2+}) in the classic host structures of positive electrode materials (layered or polyanionic compounds) is a challenge[1]. The solution could be to consider positive sulfur-based electrodes, whose electrochemical conversion process also theoretically offers very high capacities [2,3]. The first electrolyte formulations proposed are in particular the $Mg(HMDS)_2-AlCl_3$ or $MgCl_2-AlCl_3$ mixtures in ethereal solvents[4]. The presence of chlorides increases the corrosive nature of the electrolyte, which is not suitable for industrial transfer. We proposed in 2019 the use of alloys to replace magnesium with the negative electrode and thus be able to use simpler electrolytes in particular based on the salt $Mg(TFSI)_2$ [2]. This concept was validated with the alloy Mg_3Bi_2 as a negative electrode and an $Mg(TFSI)_2/DME$ electrolyte [5]. This follows from the good electrochemical behavior of certain elements of the p block (bismuth, tin, etc.) with the magnesium ions [6]. Our objective is now to improve the concept, by methodically optimizing the different components: negative and positive electrodes and electrolyte. We will present here a benchmark of the alloys Mg_3Bi_2 , Mg_2Sn and Mg_2Pb prepared by mechanochemical synthesis, and the comparison of their electrochemical behavior in a system as standardized as possible (loading of similar alloy, same electrolyte and same sulfur-carbon composite electrode, etc.). In parallel, we are also interested in protecting the Mg surface by coating of these p-block elements, through chemical or physical methods, and preliminary results will be also presented here.

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Synthesis and self-assembly of double stimuli-responsive polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(N-isopropylacrylamide) triblock terpolymers

OC13

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Fouling-resistant membranes endowed with intelligent isopores in high-areal density are highly-desired to move towards next-generation ultrafiltration membranes. Indeed, membranes tailored with smart nanochannels, able to adjust their size in response to an external stimulus such as temperature and pH, are appealing materials to efficiently prevent the common problem of fouling, considered as one of the biggest challenges in membrane technology.

To move on this way, we have synthesized for the first time well-defined pH- and temperature-double stimuli responsive polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(N-isopropylacrylamide)(PS-*b*-P2VP-*b*-PNIPAM) chains *via* reversible addition-fragmentation chain transfer (RAFT) polymerization in the presence of 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid (CDPD) as RAFT agent and 2,2'-Azobis(2-methylpropionitrile) (AIBN) as initiator at 70°C. By using our original process combining the non-solvent induced phase separation (NIPS) and solvent vapor annealing (SVA) techniques, we have produced asymmetric and isoporous PS-*b*-P2VP-*b*-PNIPAM membranes with well-ordered core-shell nanochannels, consisting of a thermo-responsive PNIPAM core embedded in a pH-responsive P2VP shell. Using optimal pH conditions, the thermo-responsive character of PS-*b*-P2VP-*b*-PNIPAM membranes was studied by measuring the permeability of the membrane as a function of temperature.

Cumulative effects of stacking faults and nanostructuring on thermoelectric properties of β -FeSi₂

OC14

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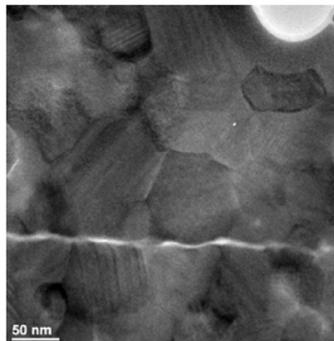
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Iron disilicide can be an outstanding candidate for thermoelectric application as it is made of abundant and nontoxic elements. Its power factor about 0.16 for pure FeSi₂ can be increased to 1.6 and 2.0 mW/m.K² after doping by Co or Al leading respectively to n-type or p-type extrinsic semi-conductor [1,2]. This values is close to the best thermoelectric material already commercialized [3]. However its thermoelectric performances still remains limited due to its rather high thermal conductivity which is about 10.3 (440 K)[4], 4.3 (425 K) and 6.2 (425 K) W/m.K for pure FeSi₂, Fe_{0.95}Co_{0.05}Si₂ and FeSi_{1.92}Al_{0.08} respectively [2]. Several routes can be investigated to scatter the phonons and then to decrease the thermal conductivity: increasing the amount of point-defect and mass fluctuation or nanostructuring.

Here, we report the nanostructuring of β -FeSi₂ by combining arc melting, mechanical milling and spark plasma sintering (SPS) which permit to obtain dense pellets (>93%) with a mean crystallite size about 50 nm (0.25 % micro strain). The thermal conductivity of nanostructured pure sample is then reduced from ~40 % to ~30 % in the temperature range 300K – 673K. The nanostructuring effect on the thermal conductivity of doped samples will also be presented as well as the impact of both, the nanostructuring and the stacking faults on the thermoelectric performances. The phonon scattering mechanisms will be presented using the Callaway's model in order to relate the effect of point-defect/mass fluctuation and of the grain boundaries on the decrease of the thermal conductivity.



TEM image of nanostrutured β -FeSi₂

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Organosilicon PECVD films for BTEX gases detection

OC15

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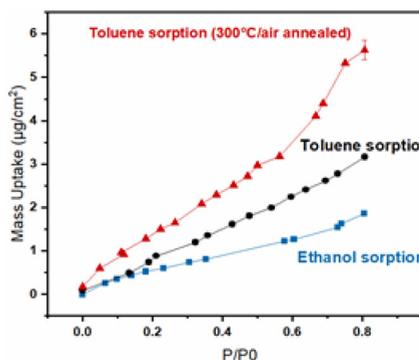
Plasma organosilicon deposited films have shown an important affinity towards harmful volatile organic compounds (VOCs), specifically BTEX gases (Benzene, Toluene, Ethyl-benzene and Xylene) [1]. Thus, these membranes are promising candidates for the detection or separation (from air and water) of such gases [2,3]. The adsorption of species at the surface of the film, as well as their absorption and diffusion within the material bulk are the two main mechanisms that condition performances of both a selective sensor or a permselective membrane.

Therefore, the determination of the bulk and the surface compositions and the chemical architecture is necessary.

This work concerns thin films prepared by microwave Plasma Enhanced Chemical Vapor Deposition (MW-PECVD) [4] under various plasma conditions, using Hexamethyldisiloxane (HMDSO) as precursor. It presents the comparison between bulk and surface compositions of organosilicon films prepared by (PECVD) using a methodology that combines experiments, chemical characterization and DFT calculations. In addition, the effect of the plasma parameters, such as plasma power (W) and the HMDSO flow rate (F), on the sorption of BTEX gases have been studied. With these aims, organosilicon

films were characterized by Fourier transform-infrared (FTIR) and ^{29}Si Solid-state NMR spectroscopies to figure out the bulk composition. X-ray photoelectron spectroscopy combined with DFT calculations led us to determine the surface composition of PECVD organosilicon films. The sorption of BTEX gases was studied by Quartz Crystal Microbalance (QCM) and ellipsometry coupled with vapor sorption.

As main striking results, this work has allowed us to figure out the ideal plasma conditions to elaborate organosilicon films for BTEX sensors applications. In optimized plasma condition (especially after post-thermal treatment), there is a noticeable difference of the mass of the organosilicon film due to ethanol and toluene sorption determined by QCM as shown in the figure below.



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Crystallographic and DFT investigation of weak CH...O hydrogen bonds in as-synthesized zeolitic materials

OC16

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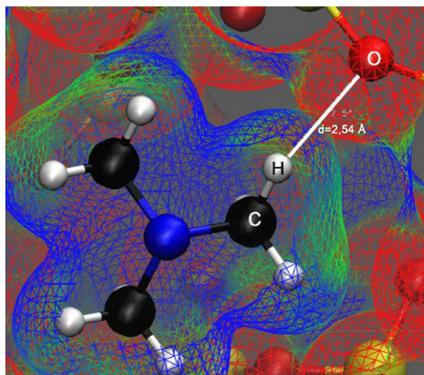
Zeolites - a large family of microporous crystals - are nowadays of great interest for the synthesis and improvement of their properties and industrial applications (heterogeneous catalysis, adsorption, separation). The organic structure directing agent (OSDA), often used in the zeolite synthesis, influences the structural organization of the silica framework and the inside distribution of other ions, such as Al^{3+} , Na^+ , K^+ , F^- , etc. In order to understand OSDA-zeolite molecular interactions we have been investigating these structures with DFT based on theoretical approaches and experimental NMR methods.

Recently, we were able to identify the existence of weak C-H...O hydrogen bonds (HBs) in zeolites with simple and complex topologies (AST and MFI) [2,3]. These intermolecular interactions - known as weak interactions compared to the classical hydrogen bonds [4] - have been overlooked in the field of zeolites until now. This is despite the fact that they can play an important role in the stabilization of zeolite-OSDA assemblies. We have thus extended our study to a series of 5 zeolites.

In this presentation we will discuss our most recent finding about HBs identifications in zeolite-OSDA assemblies with different OSDAs and topologies (AST,ITW,MFI,STT,TON).

From the DFT optimized models, we have retrieved various geometrical parameters (distances: H...O and C...O, angles: CHO and COSi). This allows probing the presence of the HBs between the OSDA and the silica framework. In addition, we will discuss the location of HBs relative to N and F atoms. Furthermore, to understand how these HBs couple to the well-known classical electrostatic interactions we have computed Mulliken charges and the electrostatic potential maps (figure). These electrostatic potentials maps show a high color contrast between the OSDA and the framework at the HBs area which will be also discussed.

All these results point to a ubiquitous presence of HBs whose role is investigated thanks to additional experimental and theoretical approaches.



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Defects and their influence on the thermoelectric properties of materials: an *ab initio* study

OC17

Philippe JUND

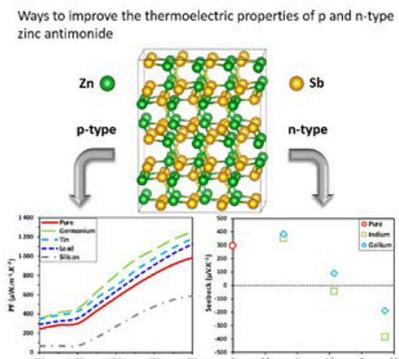
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For thermoelectric applications, *ab initio* methods generally fail to predict the transport properties of materials because of their inability to predict properly the carrier concentrations that control the electronic properties. In this presentation, a methodology to fill in this gap is shown and applied to different important materials for thermoelectric applications (antimonides (ZnSb), half (NiTiSn) and full Heusters (Fe₃VAI)).

For that we use a thermodynamics based definition of the formation energy of defects and show that the main intrinsic defects act as donors or acceptors of electrons and are responsible of the electronic properties of the experimentally-called “pure” materials. Using the same methodology we show how first principles based calculations can predict which dopants (treated like defects) are best to improve the properties of a given material. When possible we determine all the thermoelectric properties (including the thermal conductivity since defects also impact the phonon transport) and an overall correct agreement with experiments is obtained.



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Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica

OC18

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The creation of novel functional materials is a technological need and a scientific challenge for the production of innovative systems able to face the requirements of many application fields. Cooling technologies are useful in many fields related to daily life (domestic refrigeration, computer cooling, air conditioning ...) as well as high technology (cooling of optoelectronic devices, superconducting devices, thermal management of electronic devices ...) In this, all-solid technologies based on the thermoelectric effect such as Peltier cooling devices represent a real alternative, as they have no moving parts, are compact and reliable. Despite the technological advance of the system, large-scale applications of Peltier cooling devices have been limited so far, mainly due to their insufficient performance and their rather high cost. While typically used alloys can be toxic and expensive, Bi_{1-x}Sb_x alloys have a strong potential for cooling applications. Therefore, the insertion of the metallic component inside of a porous structure, such as zeolite channels and silicas pores, could improve the thermoelectrical properties with respect to the bulk material. One of the systems that are explored is formed by silica nanotubes in which Bi metal is inserted to form nanowires. Among the many parameters, the channel arrangement and dimensionality are of crucial importance in obtaining metal nanowires affecting the outcome performances of the composite. The specific aims are the decrease of thermal conductivity and the increase of the Seebeck coefficient by exploiting the quantum confinement of the metal phase. Besides metals, also organic molecules are of interest when confined in a zeolite channel. The possibility of insertion and reaction of molecules inside an organized scaffold can lead to new properties of both the inorganic host structure and the organic guest molecule. Exploiting the wide variety of the organic functions, ranging from multiple C-C bonds to the presence of heteroatoms, a multitude of composites can serve to the different purposes of the ever-growing demand of modern efficient materials. In particular, the use of unsaturated hydrocarbons monomers allows for the formation of polymers within the porous structure exploring different ranges of temperature and pressures. These hybrid systems are of interest for applications such as gas sensor materials exploiting the possibility to form conducting polymers. A promising one is found in the AlPO-54/polyphenylacetylene (PPHA) system for which the polymerization of the PhA molecules was obtained. The systems are studied and characterized by infrared, Raman and nuclear magnetic resonance spectroscopy, transmission electron microscopy and X-ray neutron diffraction both at ambient pressure and at high pressure to provide a rich description of the host-guest interactions.

Au and Au-Ag electrocatalysts for glycerol oxidation and co-production of hydrogen

OC19

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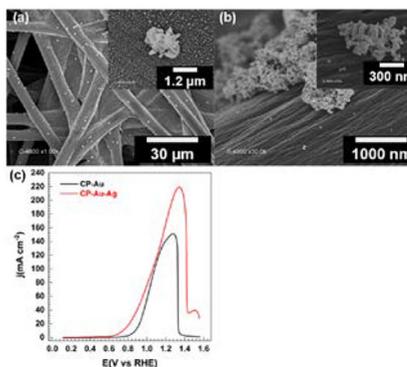
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The electrocatalytic oxidation of organic molecules is emerging as an effective method for low-energy input hydrogen production in membrane reactors. Glycerol is a promising hydrogen source due to a given low thermodynamic barrier of its electrooxidation [1] in alkaline medium, the possibility to co-generate valuable C3-compounds [2] and low overall cost.[2] Our research project thus aims to develop electrocatalysts based on monometallic Au and bimetallic Au-Ag nanoparticles [3] for the electrooxidation of glycerol.

We have developed a gamma irradiation method to deposit gold nanoparticles by reducing Au(III) salts. Using this radiolytic method, fine spherical nanoparticles as well as unusual flower-shaped particles were obtained directly on a carbon electrode (Figure a). This type of electrode allowed performing electro-oxidation of glycerol that can be modulated by varying the concentration and nature of the reducing agent, and to exceed the performance of AuNPs obtained by simple electrodeposition 2 to 3 times. In addition, gamma irradiation of aqueous solutions with mixed Au(III) and Ag(I) salts allowed the deposition of Au-Ag bimetallic nanoparticles (Figure b) with improved catalytic activity for glycerol oxidation, as observed by cyclic voltammetry in Figure c. We studied the best Au:Ag molar ratio to improve the electrocatalytic activity of the electro-catalysts, with the perspective of determining their selectivity in an H₂ electrolyzer.



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3D printing of a new generation of structured polymer derived ceramics

OC20

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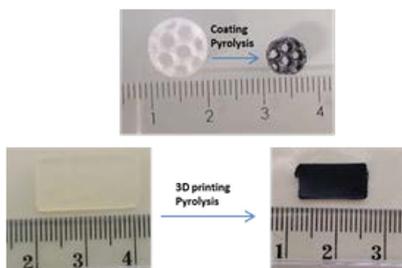
Additive manufacturing (AM), also known as 3D printing is in majority applied to produce polymeric, metallic, and recently ceramic components. The main advantage is the ability to produce complex-shaped ceramics difficult to produce *via* the conventional shaping techniques. In this work, we show that Polymer-Derived Ceramics (PDCs) can be processed using two different 3D printing technologies: i) Fused Deposition Modeling based on the fusion of a thermoplastic polymer (FDM) [1] and ii) stereolithography based on photopolymerization (SLA) [2,3]. The main advantage of the PDCs route is that the composition of preceramic polymers can be controlled

at molecular scale and preceramic polymers can be shaped into desired forms by polymer processing techniques and converted into ceramics at relatively low temperatures. Such ceramics exhibit interesting properties such as good mechanical stability, oxidation and creep resistance as well as high chemical stability in particular in the case of non-oxide systems such as SiC, Si(B)CN... [4,5]

In the first AM approach, complex honey-comb shaped Si-based ceramics were generated using the replica approach. The preceramic precursors were infiltrated into a cellular 3D printed PLA template. After pyrolysis and template removal, well-defined cellular architectures were generated and characterized.

In the second approach, the direct printing of different photosensitive preceramic polymers was performed. Tubular and planar shaped membranes were printed for water filtration.

The chemical composition and structure of the preceramic polymers (characterized by solid-state NMR and FTIR spectroscopies) as well as the printing parameters were optimized generating thus highly precise porous planar and honey-comb shaped ceramics. Their structure was characterized by SEM, EDX and 3D microscopy. For both approaches and despite the weight loss occurring during the polymer-to-ceramic conversion, the 3D ceramics did not collapse and retained a suitable strength for handling and potential use as catalyst support and membrane materials.



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CO₂ methanation over V-promoted hydrotalcite-derived nickel catalysts for CO₂ methanation: on the effect of the catalyst preparation method

OC21

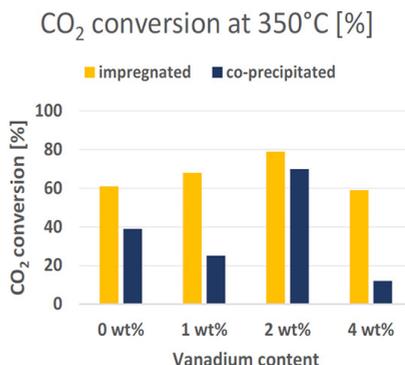
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In order to decrease the CO₂ emissions into the atmosphere, efficient ways for its utilization are under development [1]. Catalytic processes designed for this purpose are thus gaining significant attention. Among them, one of the most mature is the CO₂ hydrogenation to methane.[2] Alumina-supported Ni-based catalysts are the most commonly studied for CO₂ methanation, due to their low price, high availability, and good catalytic performance.[3] However, these catalysts easily deactivate due to coke formation and metal sintering.[3] Those drawbacks can be partially overcome by promoting the catalysts with elements, such as La, Fe, Co that can provide stronger metal-support interaction to limit deactivation.[4] Another key parameter for providing good stability is the way in which the catalyst was synthesized. Indeed, the synthesis method influences metal-support interaction by improving dispersion.[5] In this work, two series of vanadium-promoted nickel hydrotalcite-derived catalysts were compared in terms of synthesis method. Nickel impregnated V/Mg/Al hydrotalcite-derived materials have already shown their promising results in CO₂ methanation.[6] These are compared to the novel catalysts prepared by a co-precipitation method for the synthesis of hydrotalcites with simultaneous addition of all precursors. This resulted in the formation of brucite-like layered structure.[7] The co-precipitation method was used to synthesize a series of catalysts containing ca. 15 wt% of nickel, and 1, 2, or 4 wt% of vanadium in a freshly synthesized sample. Subsequently, both series were characterized by using H₂-TPR, CO₂-TPD, XRD, low-temperature N₂ sorption, and tested towards CO₂ methanation at GHSV=12,000h⁻¹. Additionally, impregnated series was examined with XANES, and so-precipitated series with HRTEM. In both series, the best catalyst for CO₂ methanation was the one containing 2 wt% of vanadium. This high activity may be directly linked with the most optimal content of basic sites and small crystallite size of Ni⁰. Moreover, the materials showed 99% selectivity towards methane formation. On the contrary, the other vanadium-promoted materials tend to form CO at temperatures below 350°C. This latter result suggests that reverse water-gas shift reaction (RWGS) takes place during the CO₂ methanation process.



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Improvement of mechanical and microstructure of poly(lactic acid) based blends for biomedical applications

OC22

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Introduction

Poly(lactic acid) (PLA) is the most used bio-based polymer. Its physical, chemical and mechanical properties make it possible to replace petroleum-based polymers for some applications (packaging, medical, textile fiber). However, neat PLA is very stiff and relatively brittle without additives. Hence, its mechanical properties have to be improved and blending with other biopolymers is a promising strategy to achieve this objective.

The aim of this work is to design biocompatible polymers compositions achievable by FDM additive manufacturing allowing a compromise between ductility and tensile strength for use in the medical field. We focused on PLA and Poly(β -hydroxybutyrate) (PHB) blends with a multi-functional epoxy as compatibilizer [1] and a plasticizing [2] agent. Experimental

Poly(lactic acid) Ingeo™ biopolymer was provided by NatureWorks, USA. PHB P209E was supplied by Biomer, Germany. Multi-functional epoxy Joncryl® ADR-4468 was provided by BASF, Germany. Dibutyl sebacate NF was provided from MERCK, Germany. The blends were prepared in a 900 mm twin screw extruder at 185°C. PLA, PHB and plasticizer were physically blended and Joncryl® was added at molten state. PLA / PHB mixtures were produced at different ratios. The plasticizer was added at 10wt% and 20wt% and the Joncryl® was added at 4wt% and 8wt% in the PLA / PHA mixture. Specimens were processed through injection molding to perform tensile tests. Firstly, selected formulations were processed through FDM additive manufacturing and optimized using design of experiments (DOE) method.

Results and discussion

To achieve a compromise between ductility and tensile strength, PLA, PHB, compatibilizer and plasticizer were blended together. Using the DOE method, we obtained a range of mechanical properties (Figure 1 above). The ANalysis Of VAriance (ANOVA) made it possible to establish that the second order polynomial model was significant and thus giving the possibility of optimizing all the mechanical characteristics studied by precisely adjusting the rate of the different components. In practice, the control points of the formulations, independent of those contained in the experimental matrix, do not corroborate the predictive phenomenological model. To understand this difference despite a true predictive model, characterizations of binary system were performed. The corresponding results could establish that, under the same extrusion conditions, PHB did not react with Joncryl®. This was ascribed to the processing conditions of the mixture and solved by increasing the extrusion reaction time and decreasing the processing temperature to avoid PHB degradation. These results could highlight the interest of specific addition stages of components on the mechanical properties of the final material. A second study, aiming to define the more relevant sequences of addition, in order to achieve the mechanical results expected in the DOE, is in progress.

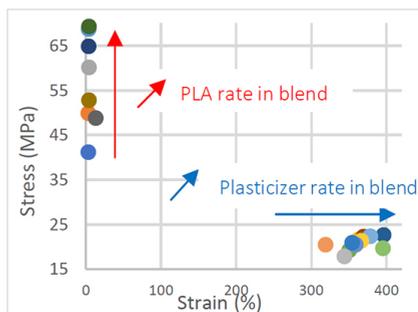


Fig 1: Results of the stress as a function of

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Elaboration of silica ceramics by indirect additive manufacturing and aqueous gelcasting

OC23

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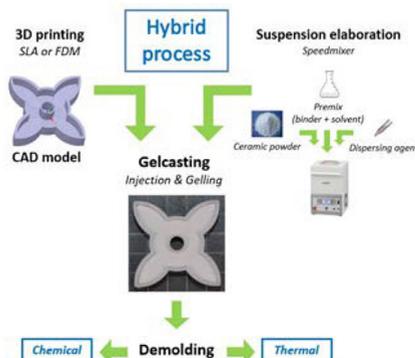
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The "gelcasting" process developed in the 1990s by Omatete and Janney [1], overcomes the disadvantages of the classical production of ceramic parts by the ceramic injection molding (CIM) method: a relatively long debinding time and a high cost for the realization of the tools used, making it impossible to manufacture small series of parts at a competitive price [2]. However, most of the studies relating to the manufacture of ceramic parts by gelcasting show that the green bodies are demolded before drying and sintering using silicone or metal molds that can be separated into several parts. In the case of complex shapes, demolding is a critical step. It cannot be carried out mechanically and it is necessary to destroy the mold thermally or chemically.

The combination of additive manufacturing of molds with the gelcasting process allows the production of complex parts [3,4]. Despite the fact that many articles deal with the production of ceramics from gelcasting, very few are devoted to the thermal or chemical demolding of the parts. Moreover, among all the literature research carried out on the manufacture of ceramic parts using the gelcasting process, the vast majority of studies concern the use of alumina powders and very few are those dealing with silica powders. To our knowledge, no study has yet been carried out on obtaining silica ceramic parts by combining gelcasting with the additive manufacturing of molds and by chemical demolding. This hybrid process was used in this study to fabricate ceramic parts of complex geometry from an aqueous ceramic suspension with a high silica filler content (> 50%vol) and a low viscosity (< 1.5 Pa.s) allowing its injection into molds printed by Stereolithography Apparatus (SLA) and Fused Deposition Modeling (FDM). The gelling and curing of the green parts are ensured by the use of the MAM/MBAM low toxicity gelling system. The evolution of gelling kinetics as a function of temperature as well as initiator and catalyst content is presented in this study. The rheological properties of the suspensions as a function of the loading rate are studied and the advantages and disadvantages of thermal or chemical demolding are exposed. The use of FDM PLA molds allowed them to be dissolved in a dichloromethane bath without damaging the raw parts, unlike SLA printed PLA molds which cause mechanical stress during removal. Nevertheless, the printing resolution of these FDM molds is not as high as for the SLA process, inducing surface defects on the parts. Thermal demolding obtained by the SLA process with a commercial burn-out resin has made it possible to obtain dense ceramic parts with a good surface finish. However, the need to dry before demolding is a bottleneck for obtaining parts with even more complex geometries. The use of chemical demolding makes it possible to avoid this critical step, but it is necessary to improve the printing resolution of the molds.



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Encapsulation of bio-inspired Mn complexes in mesoporous silica nanoparticles with improved biocompatibility for the regulation of oxidative stress

OC24

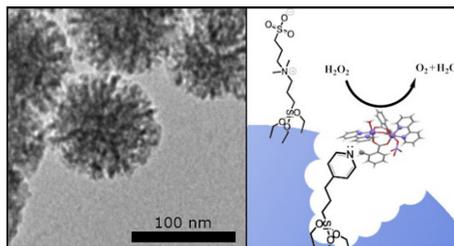
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Nature remains a major source of inspiration for designing of catalysts with great interests. Unfortunately, most of these bio-inspired catalysts are inactive in water because of instability or insolubility. This is the case for the bio-mimics of the Mn-catalase (Mn-CAT),^[1] an enzyme involved in the regulation of oxidative stress. One may solve this problem by recreating the confinement brought by the 3D-structure of the proteins through the incorporation of these catalysts inside the pores of mesoporous silica nanoparticles (MSN).^[2,3] Accordingly, our hybrid MSN's contain two organic functions: 1,4-pyridine selectively anchored on the internal surface to fix the bio-inspired Mn complex, and sulfobetain zwitterion on the external surface to ensure the biocompatibility and avoid the flocculation.^[4] The material synthesis was adapted from a previous work using cetyltrimethylammonium tosylate (CTATos) as surfactant and triethanolamine (TEAH₃) as catalyst for the sol-gel reaction.^[5] A series of nanoparticles with various amounts of organic functions was synthesized. They present an unprecedented colloidal stability in the biologic PBS buffer, mimicking the ionic media of blood while the anchored Mn complexes exhibit an excellent catalyze activity probed by the dismutation of hydrogen peroxide (H₂O₂) in aqueous media. These results are very promising for biomedical applications in which oxidative stress regulation is at stake.



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Chemical and electrochemical processes in "Water-in-salt" electrolyte

OC25

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Superconcentrated aqueous electrolytes, called water-in-salt (WIS), have recently emerged as a new class of electrolytes with salt concentration as high as 21 molal (*i.e.* 21 moles of salt per kg of water) of bis(trifluoromethylsulfonyl)imide (LiTFSI) [1]. These electrolytes are currently attracting major interest, especially for the trending development of aqueous rechargeable batteries¹. Owing to this ultrahigh salt concentration, these electrolytes have only a small amount of free water. Consequently, the electrochemical stability window of water is wider than the predicted thermodynamic value of 1.23 V. It has been highlighted that the hydrogen evolution (HER) and oxygen evolution (OER) reactions are pushed to more negative and positive potentials, respectively [2]. Nevertheless, even if this concept has been proven, decomposition mechanisms for water-in-salt electrolytes are not well understood yet. On one hand, the reductive stability of water-in-salt has been attributed to the formation of a solid-electrolyte interface at the anode [3,4]. On the other hand, the shift of the oxygen evolution reaction potential has been explained by the presence of large hydrophobic anions that blocks access of water molecules to the electrode surface [3]. However, we hypothesized that different complex phenomena such as water oxidation, electrochemical oxidation of TFSI anion, as well as TFSI anion decomposition may occur at high positive potential (Fig. 1). Thus, in this study we investigated chemical and electrochemical processes occurring at high potentials by combining three complementary electrochemical techniques (cyclic voltammetry, rotating ring-disk electrode and differential electrochemical mass spectrometry) and X-ray photoelectron spectroscopy. We showed that not only electrochemical water oxidation occurs but that different processes such as a combination of an electrochemical reaction (water or TFSI oxidation) and chemical reaction (TFSI decomposition) can take place. Finally, we demonstrate that the redox processes involved during the OER led to the formation of a film at the electrode surface.

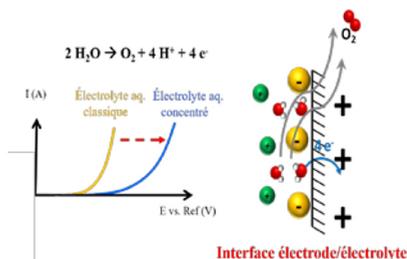


Figure 1) Schematic illustration of the interface electrode/electrolyte at high positive potential.

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Folding of phosphodiester-linked donor-acceptor oligomers into supramolecular nanotubes in water

OC26

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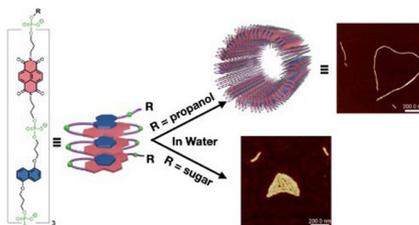
The tridimensional structuration of supramolecular assemblies has a strong importance on their biophysical properties and ultimately their functions whether they are natural (DNA, proteins) or synthetic (molecular machines, polymers). In the pursuit of new folded backbones, it has now been over three decades that foldamers have been studied. Foldamers are linear artificial oligomers able to fold into secondary structures stabilized by non-covalent forces: hydrogen bonds, π - π or σ - π interactions or van der Waals forces.[1]

They constitute new tools for developing biologically active synthetic molecules or new hybrid materials.

In this context, we have been developing the synthesis of water soluble DNA-inspired foldamers [2] built from 1,5-dialkoxynaphthalene (DAN) and 1,8,4,5-naphthalenetetracarboxylic diimide (NDI) motifs. Both aromatics are stabilized by an electrostatic complementarity interaction (donor/acceptor) known as *charge-transfer*. [3]

From newly synthesized DAN and NDI phosphoramidites, foldamers were synthesized and studied by UV-Visible and fluorescence spectroscopies. TEM and AFM imaging showed the formation of nanotubes of hundreds of nm in length and about 10 nm in diameter. [4]

We used the same backbone of alternated DAN and NDI aromatic with at each extremity a sugar for interaction with lectin. The goal is to obtain new sugar-decorated nanotubes able to exhibit a strong affinity for the bacterial lectin thanks to a glycocluster effect leading to new antibacterial agents for health applications.



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Biomimetic protein imprinting on magnetic particles using amino acid-based hybrid blocks

OC27

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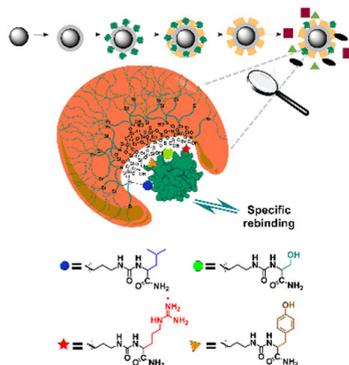
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By carrying out the polymerization in presence of a target molecule (Scheme), molecular imprinting offers the possibility to create biomimetic synthetic materials with molecular recognition properties similar to natural receptors in terms of affinity and selectivity [1,2]. Those materials are actually referred as MIP (Molecularly Imprinted Polymers) and they were first developed in silica matrix. At the beginning of the 1970s, the bigger versatility in terms of organic functional monomers triggered the transition to organic polymerization approaches [3].

Nevertheless, when complex and fragile templates such as protein are selected, the use of an inorganic polymerization approach presents several advantages compared with the traditional protocols of organic MIPs. For example, the sol-gel chemistry is performed under protein compatible conditions in terms of solvent (water instead of traditional low polarity organic solvents) and temperature (room temperature instead of traditional 60°C or higher). It offers, therefore, a simple, versatile, cost effective, biocompatible and environmentally friendly alternative to organic MIPs.

However, two main challenges have to be tackled to get protein MIPs by sol-gel approach: the pH of the reaction and the lack of diversity of functional monomers [4]. We propose then a biomimetic approach using silylated amino acids (AA) as hybrid functional monomers. The basic protein cytochrome C (p.I 9.6) was chosen as a model to prepare MIPs on the surface of silica core-shell magnetic particles. We compared the efficiency of the MIPs obtained by polymerization of common cationic and hydrophobic precursors (3-aminopropyltriethoxysilane and n-propyltriethoxysilane) with the ones obtained from functional monomers mimicking the arginine and leucine. At last, we used tyrosine and serine monomers which are the most common AA found in antibody epitope for protein recognition [5]. The efficacy of all the types of MIPs was assessed by quartz-crystal microbalance (QCM-D). The promising results obtained by this biomimetic approach based on inorganic-bioorganic polymers, open the doors for the development of imprinted devices for specific protein recognition.



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Artificial nucleation sites and the study of solvation structures in electrolytes for Lithium metal batteries

OC28

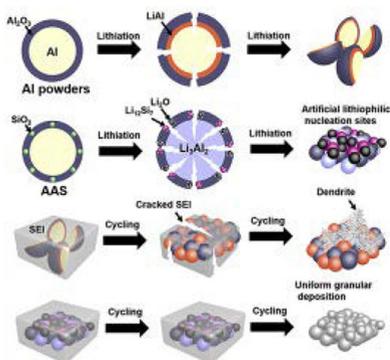
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Owing to the ultra-high specific capacity (3860 mAh g^{-1}) and the ultra-low redox potential (-3.04 V vs. S.H.E.), Li metal anodes paired with high-capacity cathodes (e.g., S , O_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, etc.) is viewed as a promising route to realize next-generation high-energy-density Li metal batteries (LMB). However, uneven nucleation and fragile solid electrolyte interphase (SEI) restrict the practical application of LMB. [1] Herein we propose an Al core- Al_2O_3 - SiO_2 (AAS) shell to form abundant artificial nucleation sites and robust SEI films by enlarging Al pulverization strategy. The AAS coated separator could extend the life-span of a Li||LiFePO_4 cell to 645 cycles with a high CE of 99.2% in the carbonate electrolytes. Based on this, we further studied on the connection between solvation structures (vital for forming SEI film components) in various carbonate electrolytes and the Li metal deposition morphology. The compact and smooth electrochemical deposited Li morphology could be achieved by adjusting the ratio of contact ion pairs (CIP) to aggregates (AGG) in electrolytes. This work demonstrates artificial nucleation sites and the study of solvation structures in electrolytes could improve cycling performance and give a guiding effect respectively for stable high-energy-density LMB.



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Light photodynamic therapy and photochemical internalization of siRNA

OC29

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We report the use of Periodic Mesoporous Ionsilica Nanoparticles (PMINPs) as versatile nano-objects for imaging, photodynamic therapy (PDT), and efficient adsorption and delivery of siRNA into breast cancer cells. Mesoporous ionsilica nanoparticles are well known for several advantages: high specific area and uniformity of both size and shape of pores. In order to confer to these nanoparticles PDT and siRNA photochemical internalization (PCI) properties, a porphyrin derivative was integrated into the ionsilica framework.

For this purpose, we synthesized PMINPs *via* hydrolysis - polycondensation procedures, starting from oligosilylated ammonium and porphyrin precursors. The formation of these nano-objects was attested by transmission electron microscopy. The formed nanoparticles were then thoroughly characterized *via* solid state NMR, nitrogen sorption and dynamic light scattering. The spectral properties of these nanoparticles were also studied using UV-Vis and fluorescence spectroscopy, attesting the successful incorporation of the porphyrin derivative.

Our results indicate the formation of highly porous nanorods ($1015 \text{ m}^2 \text{ g}^{-1}$) with $108 \pm 9 \text{ nm}$ in length and $54 \pm 4 \text{ nm}$ in width. A significant PDT effect of type (I) mechanism ($95 \pm 2.8\%$ of cell death) was observed, due to an important ROS production upon green light irradiation (15 min at 545 nm , 34 J cm^{-2}) in nanoparticles treated-breast cancer cells. Zeta potential measurements of PMINPs revealed the presence of positive surface charges ($+35.8 \text{ mV}$), which promoted the complexation of siRNA. The electrostatic complexation of siRNA was then verified by electrophoresis gel retardation assay. Furthermore, PMINPs formed stable complexes with siRNA (up to 24 hours) and were efficiently internalized into the cells after 4 hours incubation mostly with energy-dependent endocytosis process. The PCI effect was obvious under green light irradiation (5 min at 545 nm , 11.3 J cm^{-2}) and successfully led to $83 \pm 1.1\%$ silencing of luciferase gene in luciferase expressing breast cancer cells, while no gene silencing effect was observed in the absence of light.

This work highlights the high potential of porphyrin-doped PMINPs as multifunctional nanocarriers for nucleic acids, such as siRNA, with a triple ability to perform imaging, PDT and PCI.

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^{125}Te NMR structural investigations coupled to NMR shift prediction suitable for Te containing crystalline materials

OC30

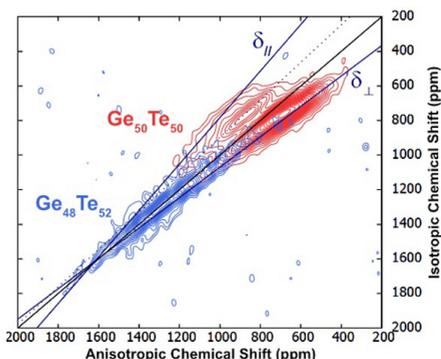
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Tellurium containing materials are used in many technological applications including conversion energy thermoelectric devices, IR optical fibers or waveguides and memory devices. They represent a family of materials of huge interest in the current societal challenges. Although GeTe has been known as thermoelectrics since 1960s, it has attracted intensive renewed attention recently. GeTe undergoes a phase transition from a high-T cubic (c-GeTe) to a low-T rhombohedral structure (r-GeTe) at ~ 720 K. Previous thermoelectric studies have mostly focused on high-symmetry c-GeTe. To date, it has been revealed that low-symmetry r-GeTe shows a thermoelectric figure of merit zT as high as that of c-GeTe making it one of the most efficient thermoelectrics for both mid-temperature (500–800 K) and near-room-temperature applications. GeTe is also a Phase Change Material (PCM) that displays very large electronic polarizabilities in the crystalline state, which were not found in the amorphous phase. Therefore, the high values of the electronic polarizability of PCMs were attributed very recently to a new type of bonding called “metavalent bonding” in the crystalline state. Investigations indicate that the findings of this special bonding is a genuine mechanism in solids and not merely an intermediate (or a combination) of covalent and metallic bonding[1]. Properties of these compounds are strongly related to presence of vacancies and structural investigations remain challenging. In this study we have evidenced that ^{125}Te NMR in natural abundance and using commercial systems at intermediate field (14T) together with NMR parameters prediction can contribute to improve understanding of electronic structure of such systems. $\text{Ge}_{50}\text{Te}_{50}$ is a typical PCM, whose structure contains germanium vacancies, even in its stoichiometric form, giving it metallic properties. We have used nominal $\text{Ge}_{50}\text{Te}_{50}$ and $\text{Ge}_{48}\text{Te}_{52}$ crystalline phases as an example to optimize the WURST-CPMG technique, a powerful technique to record wide NMR spectra which has not yet been used on ^{125}Te . The goal has been to minimize the time devoted to experiments as well as maximize the signal-to-noise ratio in order to detect small intensity signals directly linked to vacancies. Virtual Crystal Approximation (VCA) calculations performed with WIEN2K helped to interpret the NMR spectra. In addition to the WURST-CPMG technique, high resolution spectra using MAS as implemented in the pj-MAT technique (figure) has allowed us to identify the distribution of chemical shift in the high intensity contribution of the 1D spectra. The NMR spectra recorded on the samples showed that an addition of Tellurium in the stoichiometric $\text{Ge}_{50}\text{Te}_{50}$ sample leads to an important broadening of the spectrum together with a shift of the lines. According to VCA calculations it could be attributed to a distribution of concentrations of germanium vacancies in the sample and it would appear that Knight Shift but also Chemical Shift can contribute in similar proportion to the NMR line position when metavalent bonding is invoked.



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Cage-derived mesoporous silica nanomaterials

OC31

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Functional silica nanoparticles have become highly relevant materials in the fields of biology and medicine. Sub-10 nm fluorescent silica nanoparticles, known as Cdots, and developed at Cornell University (United States), have now reached phase 2 of clinical trials for cancer diagnostics. Nevertheless, modern nanomedicine techniques and their increasing complexity are still in demand for more efficient and multifunctional tools for advanced applications such as theranostics. To this end, important developments have been made in order for these nanoparticles to achieve their full potential, including chemical modification of their matrix and surface. In parallel, alternative particle morphologies such as porous nanoparticles are being investigated for their potential in targeted drug delivery strategies.

In this context, we discovered a series of new low dimensional structures derived from the sol-gel synthesis of mesoporous silica templated by surfactant micelles, including ultrasmall silica cages [1], rings [2], and 2D superlattices of silica cages [3]. Among these materials, a cage structure with well-defined dodecahedral symmetry was in particular revealed by single particle 3D reconstruction from cryo-TEM images [1]. The synthesis of these structures around hydrophobic micelles allows for the differentiated functionalization of their inner and outer surfaces with a large variety of functions,



making them an ideal cargo vehicle. For example, given recent success in the clinical translation of ultrasmall fluorescent silica nanoparticles with similar particle sizes and surface properties to these cages, one can envisage a range of new diagnostic and therapeutic probes with drugs hidden inside the cages.

In another development, silica cages were further functionalized with photoresponsive ligands for their integration with innovative 3D printing [4]. This approach enables the direct printing of mesoporous objects with programmable (micro)structures. Making use of the versatile surface chemistry and intrinsic porosity of these cages, we demonstrated the effective implementation of localized functionalities within printed parts, generating interesting perspectives for the fabrication of bioanalytical platforms.

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Analysis of ion correlation in silica nanochannels: molecular dynamics of ion distribution and potential of mean force

OC32

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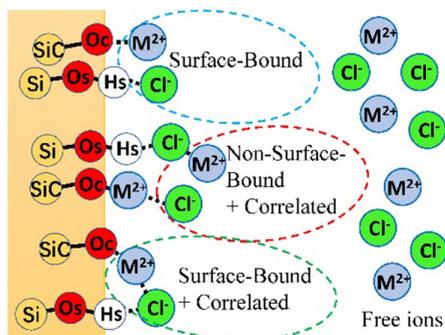
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Understanding and predicting material behaviors in contact with aqueous electrolyte solutions require detailed investigating of solid-liquid interfaces. Thanks to the contribution of molecular dynamics [1], we are now able to investigate the macroscopic concepts of solid-liquid interface directly from an atomistic description. This work presents Molecular Dynamics (MD) simulations dedicated to analyze correlations between ion and silica surface including three body effects, one particle belonging (surface site) to the surface and two (ions) to the solution. An extensive description of surface correlation situations is provided from simulations

of three alkaline earth metal chlorides (Mg^{2+} , Ca^{2+} , and Ba^{2+}) aqueous solutions at 1 mol/L in negatively charged silica nanochannels. Here, three types of ions are introduced for describing Electrical Double Layer (EDL): surface-bound, correlated, and free ions. Surface-bound ions form contact ion pairs (CIP) with surface sites which can be regarded as fixed ions. Correlated ions form CIPs with other surface-bound ions and correlated ions, we get free ions. For doing this analysis, we provide the results of McMillan-Mayer Potential of Mean Force (PMF) which give the equilibrium distances of ion pairs. By computing the association constants as well as the Mean First Passage Time (MFPT), we also found a decreasing



affinity of deprotonated silanol along with the series $Mg^{2+} > Ca^{2+} > Ba^{2+}$, while the formation of bulk $M^{2+}-Cl^{-}$ pair is in reverse order. MD simulations of negatively charged silica nanochannels show that the amount of correlated ions increases with the matching water affinity [2]. We found that 25% of non-free Ba^{2+} ions are actually non-surface-bound but correlated ions. On the silica surface, over 40% of surface-bound Ba^{2+} ions are also correlated with surface-bound Cl^{-} while other two cation systems do not show this trend. When the surface-bound ions and correlated ions are taken apart, the remaining free ions fit well the Poisson-Boltzmann (PB) equation. These results demonstrate the necessity to account for three-body associations on oxide surfaces at least for divalent ions. Combined with recent works of X-ray reflectivity [3,4] which report the $BaCl_2$ clogging in small confined silica nanochannels and which can be explained by the synergy of CIP formation and surface adsorption, this conclusion is significant for confined media study especially for pore size < 5 nm.

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Polyoxazolines nanoformulations towards an effective antioxidant delivery to prevent skin cancer

OC33

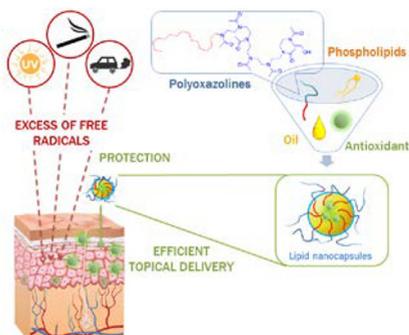
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With a surface of 2 m², the skin is the most extended organ of human body, acting as a barrier against external aggressions. Some environmental factors such as UV radiations, pollutants and tobacco still over generate free radicals within the skin layer leading to premature skin aging and potential skin cancer [1]. To reduce this enhanced oxidative stress in human skin, topical delivery of antioxidant to the epidermis offers a suitable solution. Our studies intend to address this challenging research by designing innovative nanoformulations to topically deliver antioxidant thanks to an enhanced penetration by means of lipids and amphiphilic polyoxazolines (POx) [2]. POx are bioinspired polymers with excellent biomedical properties such as biocompatibility, cytocompatibility, stealth behavior [3] and therefore constitute a suitable alternative to poly(ethylene glycol) (PEG) overuse [4]. Two main lipid based nanoformulations with POx were designed : mixed micelles [5] made of POx and phospholipids and lipid nanocapsules (LNC) [6] composed of an oily core surrounded by a phospholipids shell and a POx corona. As the results, LNC POx of 30 nm in size demonstrated an increased antioxidant loading compared to the PEG reference [6] (8 % vs 2.6 %), a high stability overtime and an efficient antioxidant activity. LNC POx were able to scavenge the excess of free radicals generated by peroxides on mice fibroblasts and by UV irradiation on human keratinocytes while maintaining cells viability. The penetration capacity of POx and LNC POx was investigated on various skin models from simple phospholipid membranes such as GUV and cells to mice ears by *in vivo* study. Grafting a fluorescent probe on POx allowed monitoring the penetration of POx and LNC POx, which insert in lipid membranes and penetrate in mice skin. LNC POx were proved to penetrate the mice epidermis and deliver the antioxidant. These results demonstrated for the first time the potential of POx for topical delivery of active molecule.



Overall, POx were proved to be an excellent alternative to PEG overuse for designing formulations and show promise for topical delivery of antioxidants into epidermis creating new possibilities for skin treatment of psoriasis or melanomas.

Overall, POx were proved to be an excellent alternative to PEG overuse for designing formulations and show promise for topical delivery of antioxidants into epidermis creating new possibilities for skin treatment of psoriasis or melanomas.

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Iron and/or titanium containing microporous silico-aluminophosphates as a novel photocatalyst for hydrogen production by water splitting process.

OC34

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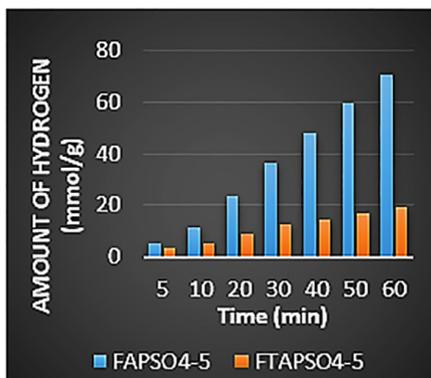


Since their first synthesis, the Silico-aluminophosphates materials proved their efficiency as a good adsorbent and catalyst in several environmental and energetic applications.

In this work, the photocatalytic hydrogen production from water splitting reactions have been conducted, under visible radiations, in the presence of a series iron and/or titanium containing microporous silico-aluminophosphates materials synthesized by hydrothermal method, using triethylamine as an organic structuring agent to obtain the AFI structure type.

These photo-catalysts were then characterized by various physicochemical methods to determine their structural, textural and morphological properties such as X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM) coupled with X-rays microanalysis, nitrogen adsorption measurements, UV-visible diffuse reflectance spectroscopy (UV-Vis-DRS), and X-rays photoelectron spectroscopy (XPS) and the analysis revealed that these materials have significant Photocatalytic properties.

The hydrogen production process has been followed by photo-electrochemical characterization (PEC). The results showed that hydrogen is the only gas produced and the reaction takes place in the conduction band where water is reduced to hydrogen. The electron recombination has also been avoided as holes are entrapped using hole scavengers. In addition, these catalysts had been shown to remain stable during reuse up to five cycles.



Acknowledgements

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Fabrication of injectable calcium phosphate cements containing polymer microspheres for drug delivery

OC35

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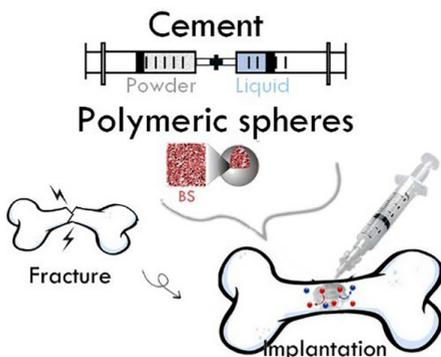


Bone is a living tissue which undergoes constant remodeling and whose performance could be altered by various diseases such as osteoporosis, fibrous dysplasia or cancer metastases... In addition to be painful for patients, these diseases lead to pathological fractures, which require multidisciplinary approaches for their treatment. In many cases, a bone substitute material is used to fix the damaged tissue and to provide a mechanical support [1]. Therapeutic arsenal is constantly supplemented with novel interventional techniques to propose alternatives, less invasive than the surgical procedure [2]. The goal of this work is to propose a combined matrix having the potential to improve drug targeting to obtain a selective accumulation in the bone lesion with tunable characteristics.

The solid mineral phase was constituted by calcium phosphates and magnesium phosphates. The cement was obtained by mixing the powder with an aqueous solution with a powder-to-liquid ratio of 0.5mL per gram of solid content. Subsequently, a range of biopolymer was evaluated to select the best candidate according to its affinity with the cement matrix. Poly (lactic-co-glycolic acid) (PLGA) was selected, ideally suited as biocompatible and biodegradable material, exhibiting a wide range of erosion times, and is FDA approved.

Polymeric microspheres were designed by double-emulsion-solvent-evaporation method. The particles were incorporated homogeneously in the powder. Different formulations (C/PLGA5 to C/PLGA30) were tested by the addition of acid poly-(lactic-co-glycolic) (PLGA) microspheres (5 to 30 wt%). The controlled porosity created by these microspheres allows a modulation of the cement degradation time and improves the osteoconduction of the substitute material. The size of microspheres and percentage incorporated in the biomaterial influences on the physico-chemical properties, as well the biological characteristics. Setting time and degradation kinetics were evaluated to be compatible with the clinical need.

Furthermore, polymeric microspheres are also used as carriers for drugs, including a bisphosphonate (BS) indicated for the treatment and the prevention of osteoporosis and breast cancer. The bisphosphonate was incorporated into the particles directly during the double emulsion step. Various protocols and initial content of drug were evaluated to obtain the best loading. Then, they were mixed with the cement matrix to evaluate the release kinetics in physiologic conditions. *In vitro* study was performed on osteoblastic cells (hFOB 1.19) to confirm materials biocompatibility. Further analysis is ongoing to test the efficiency of the composite *in vitro* and *in vivo*.



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Influence of NaCl concentration on the desalination performance of carbon based flow electrode.

OC36

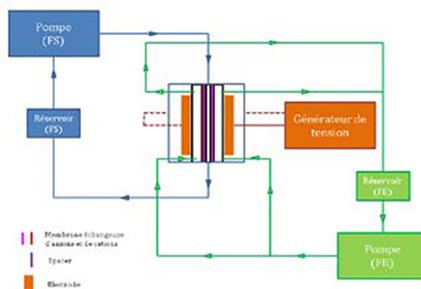
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Flow electrode capacitive deionization is a novel technology (a variant of capacitive deionization CDI) that proffers continuous desalination method based on a constant movement of polarized slurry electrode on carved channels that also stand has current collectors. Flow electrode performance is influenced by so many parameters like voltage, feed concentration, electro-conductivity of the feed electrolyte, cell geometry etc. In this study, the electro-conductivity of the feed electrode was influenced by varied amount of NaCl concentration and it effect was studied on desalination. Also, we confirmed that little concentration of salt electrolyte component of the feed electrode is sufficient to make significant difference in brackish water desalination as high as 5 g/L (85.5 mM).



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Si(B)CN/ rGO composites as an electrocatalyst for Hydrogen Evolution Reaction (HER)

OC37

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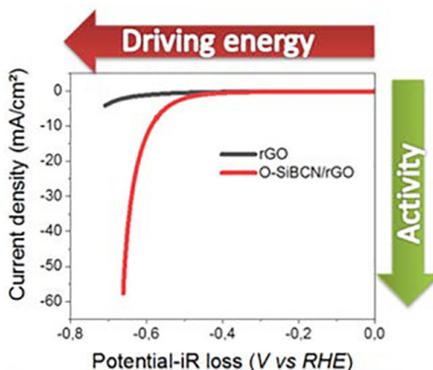
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Hydrogen, the most environment-friendly fuel with the highest energy density, is considered as a potential energy carrier for applications such as hydrogen cars and power stations. One way to produce hydrogen is *via* electrocatalytic water splitting, which still relies on catalysts with superior activity. This imposes that the catalysts for the Hydrogen Evolution Reaction (HER) – the half reaction involved in water splitting – must be thermodynamically and kinetically optimized. As we know, Platinum is the best catalyst for HER, however it is scarce, unstable and very expensive, which limit its use. Therefore, research recently was aiming to developing novel sustainable and affordable catalysts for HER.

Polymer-derived ceramics have been found recently to be eligible for electrochemistry applications [1] for energy storage. In this study, we are investigating the performance of polymer derived ceramics as electrodes for the hydrogen evolution reaction. 3D highly porous graphene-based ceramic composites were synthesized, fully characterized and assessed as electrochemically active electrodes for the hydrogen evolution reaction in acidic conditions. The polymer-derived ceramics approach combined with the hydrothermal synthesis of graphene oxide aerogels [2] was used to produce composites with a great control of the chemical composition, structure, phase distribution and porosity. Two polymer-derived ceramic systems were studied: silicocarbonitride (Si-C-N) and boron-modified silicocarbonitride (Si-B-C-N) and the composites with reduced graphene oxide (rGO) were found to be electrically conducting, mechanically strong and electrochemically active. Our results suggest that the SiBCN/rGO composites display the strongest activity with low onset potential and larger current densities thanks to a combined effect from the intrinsic activity of SiBCN and the high porosity and electrical conductivity of rGO support. This electrocatalytic activity is further improved upon oxygen doping. Remarkably, the O-SiBCN/rGO electrodes demonstrate high stability towards the production of hydrogen. This study provides new insights on the performance of PDC-based catalysts for the HER and calls for further exploration of the catalytic activity of PDC-based materials.



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A systematic rational study of the influence of the insertion of Mn²⁺ in Prussian blue nanoparticles on their photothermal properties

OC38

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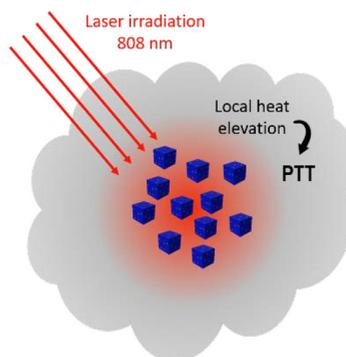
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Prussian Blue (PB) type (PB) nanoparticles are a particular family of inorganic nano-sized materials, which have been widely investigated over the last two decades due to their versatile composition, exciting physico-chemical properties and different promising applications in different fields including energy, catalysis, decontamination, sensors and healthcare. In particular, the development of PB type nano-objects in the domain of medicine like imaging and therapy has seen an extensive expansion due to several advantages like near-infrared region absorption. To improve PB therapy efficiency, Mn²⁺ insertion into its structure has been studied and several articles by other groups and by us have reported on the investigation of the photothermal efficiency of Mn²⁺-doped PB nanoparticles [1,2].

We investigated a series of Mn²⁺-Prussian blue nanoparticles Na₂Mn_xFe_{1-x}[Fe(CN)₆]_{1-y/z}·xH₂O of similar size and morphology with various amounts of Mn²⁺ synthesized through a one step procedure. We demonstrate that the Mn²⁺ substituted the Fe³⁺ up to 32% Mn content in the PB structure while for higher amounts, the PB analogous Mn₃[Fe(CN)₆] is obtained. For comparison, the post-insertion of Mn²⁺ on PB nanoparticles was also investigated and completed with Monte Carlo simulations. All obtained nanoparticles were characterized using XRD, UV-Vis, TEM, SEM-EDS, TGA, FTIR and elemental analysis.

Further, the photothermal conversion efficiency (η) of selected samples was determined showing a non-linear dependency of η with the amount of Mn²⁺ inserted and a maximum efficiency for 10% Mn. Evaluation of the cytotoxic effect of selected samples was performed on triple negative human breast adenocarcinoma (MDA-MB-231) cells. Further, the efficiency of selected samples *in vivo* as photothermal agents on zebrafish embryos xenografted with human breast cancer cell line was investigated.



Acknowledgment: This work is supported by ANR with grant number ANR-18-CE09-0012-01.

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REVERSIBLE H₂ storage *via* BCN

OC39

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The hydrogen energy and economy are highly promising. Nevertheless, one of the main issues for its full development is storage. Different methods are explored to overcome this challenge. Currently, H₂ is stored as compressed gas (200 to 700 bars) or cryogenic liquid (-253°C) implying expensive processes and notable safety risks. [1] A solid-state storage is expected to provide a safe, efficient and reversible alternative. [2]

One of the most promising candidates for solid-state sorption of H₂ is boron nitride (BN). Several structures of porous BN were reported showing its ability to reversibly adsorb hydrogen at room temperature. [3] However, the desorption takes place at high temperatures (up to 300°C) and might alter the BN structure. Accordingly, research has lately been focused on improving BN adsorption/desorption capacities, which are governed by different factors such as structural defects, carbon or metal doping, specific surface area and microporosity. [4]



In this collaborative work between ICGM and IEM, we opt for nanostructuring BN as well as doping by carbon in order to improve hydrogen storage capacities. Therefore, ammonia borane (AB) and amine-borane adducts (ABAs) RNH₂NH₃ are combined to create novel nanostructures. Other amine-borane based precursors are also explored such as ethylenediamine bisborane (EDAB). Many BN and BCN materials are already synthesized and characterized. They already showed interesting CO₂ capture capacities and will soon be studied for H₂ reversible storage.

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Development of novel strategies to target DNA methylation and histone acetylation in cancers

OC40

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Epigenetic modifications, such as DNA methylation, catalysed by DNA methyltransferases (DNMTs), or histone deacetylation, catalysed histone deacetylases (HDACs), play an essential role in the regulation of gene expression. [1] It is now clearly established that an aberrant DNA hypermethylation of the tumour suppressor gene promoter regions is associated with cancer formation and proliferation. [2] To date, two DNMT inhibitors are FDA-approved for the treatment of leukaemia. However, as nucleoside analogues, their need of DNA incorporation and their instability in physiologic media greatly limit their use. [3]

In this project we aim at designing dual HDAC and DNMT inhibitors to lay down the bases of an innovative strategy to target these epigenetic mechanisms in cancers. This strategy could be of high interest for these targets since combinations of HDACi and DNMTi are used as anticancer treatment. Furthermore, more recently, multi-target drugs have emerged as a promising therapeutic strategy. [4]

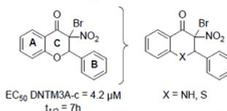
To do so our first goal was to identify relevant non-nucleoside DNMT. Our group previously identified a novel class of DNMT inhibitors: 3-halo-3-nitroflavonones. [5] Despite promising results, these compounds showed moderate stability in physiological conditions. In order to overcome this lack of stability we designed and synthesized new flavonoid analogues:

3-halo-3-nitrothio-/aza-flavonone. With these compounds although no improvement of the stability in physiologic media was observed, a micromolar range inhibition activity was measured *in vitro* on purified DNMT3A-c using an in-house DNA methylation fluorescence assay.

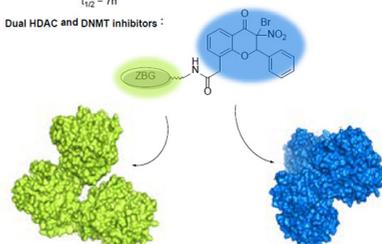
In a second part, with the library of non-nucleoside DNMTi in our hands, we developed new dual HDAC-DNMT inhibitors based on 3-bromo-3-nitroflavonones. As pharmacophore for HDAC inhibition, we selected hydroxamic acid and benzamide since they constitute the zinc-binding group (ZBG) of two intensively studied HDACi, Vorinostat and Entinostat. Previous structure-activity relationship studies showed that functionalisation of position 8 of flavonones was not deleterious for inhibition activity and will thus be used as anchoring point of the ZBG. We showed that corresponding dual inhibitors displayed micromolar IC_{50} in KG1 cells and induced DNA damage.

These results highlight the interest to simultaneously target HDAC and DNMT. Through this project, we identified an innovative strategy to target with a single molecule DNA methylation and histone acetylation. Our results could pave the way to the discovery of innovative epigenetic targeting in cancers.

New non-nucleoside analogues : 3-halo-3-nitroflavonones



Dual HDAC and DNMT inhibitors :



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Modified titanium oxide for green hydrogen production by electro-photocatalysis

OC41

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Hydrogen is an ideal energy carrier to offset the use of fossil fuels. However today more than 96% of it is produced by reforming methane which is a thermochemical process using fossil fuels. To overcome this problem, one of attractive solution is electro-photocatalysis, which combines electrolysis and photocatalytic dissociation of water. The similarity between photocatalysis and photolysis of water lies in the use of semiconductor material as a photoelectrode. Unlike photolysis, the charges of the exciton in the photocatalysis process will be able to leave the semiconductor and circulate through the external circuit. With this solution, we can produce green hydrogen using sunlight and water as the only resources.

From titanium oxide, a valued photocatalytic material due to its appropriate optoelectronic properties, high availability and chemical stability, as well as its low cost and non-toxicity [1], we have developed by sol-gel dip-coating method innovative photo-anodic materials. Concerned about environmental issues, we have prepared TiO_2 -based materials with green surfactant and modified them by two different methods with the aim of improving their electro-photocatalytic properties.

In the first approach, TiO_2 thin layers have been combined with cobalt oxide to create a n-p heterojunction. This junction between a n-type semi-conductor (TiO_2) and a p-type semi-conductor (Co_3O_4) is theoretically able to move light absorption of TiO_2 in the visible region and also to decrease the recombination of electrons-holes pairs [2].

In the second approach, we have synthesized sub-stoichiometric titanium oxides such as Ti_4O_7 or Ti_5O_9 , called Magneli phases, known for their high electronic conductivity [3]. They have been obtained by the carbo-reduction route using green surfactant as carbon source.

A structural characterisation of both families of materials by EDX, XRD and Rietveld refinement has confirmed the existence of the different targeted compounds, which enables to validate both approaches. Concerning the heterojunction approach, comparison of UV-visible spectra of TiO_2 and $\text{Co}_3\text{O}_4/\text{TiO}_2$ has revealed a noticeable absorption shift through the visible region adding Co_3O_4 as expected. Electrochemical impedance spectroscopy, cyclic voltametry and photo-current measurements performed under visible/UV light irradiation have proved enhanced photoelectrochemical performances adding Co_3O_4 .

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Nanodiamond-based organosilica nanoparticles for two-photon imaging and antibacterial photodynamic therapy

OC42

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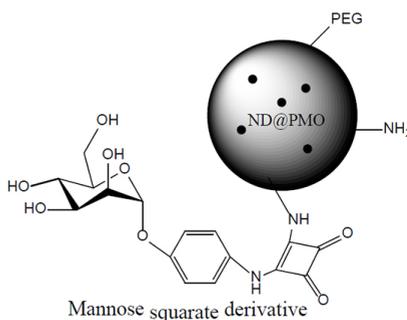


Nanodiamonds (NDs) with exceptional optical, thermal and mechanical properties emerged on the global scientific scene, especially in biomedicine and bioanalysis fields. Nanodiamond-based periodic mesoporous organosilica nanoparticles (ND@PMO NPs) recently displayed *in vitro* photosensitizing capability on MCF-7 breast cancer cells with two-photon excited photodynamic therapy (TPE-PDT) and fluorescence properties for two-photon imaging (TPI) [1,2]. With no silica source, these nanoparticles synthesized through sol-gel condensation in mild conditions were holding good biocompatibility due to their PMO-based shell.

In this work, we described ND@PMO NPs with various size distribution depending on the nature of hydroxylated NDs and organosilica precursor employed. Some NPs were further modified. First, amino-silane and PEG-silane were grafted, the last bringing antifouling properties and suspension stability. Then, a mannose squarate derivative (MAN) was anchored through the amino function to target bacterial infections by specific binding onto FimH lectins of bacteria membrane [3,4].

FTIR spectra displaying ND, PEG, MAN and siloxane network characteristic bands confirmed the structure, reinforced by surface zeta potential shift from very positive values (amino groups, > 20 mV) to negative values (mannose hydroxyl groups, < -20 mV). UV-vis absorption spectra regression allowed determining the MAN-grafting rate. First biological studies were conducted to assess the potential of different ND@PMO samples.

The long-term objective is to apply these carbohydrate-grafted NPs to antibacterial purpose, especially wound healing, by performing TPI and synergistic TPE-PDT and chemotherapy by the mean of vancomycin loading into PMO pores.



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Catalytic activity of natural clinoptilolite and MWW-type zeolite modified with iron in selective catalytic reduction of nitrogen oxides with ammonia (NH₃-SCR)

OC43

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Selective catalytic reduction with ammonia (NH₃-SCR) is one of the most important industrial processes for the abatement of nitrogen oxides (NO_x) [1]. The most common catalyst of the technology is V₂O₅ supported on TiO₂ and promoted with MoO₃ or WO₃. Despite satisfactory activity above 300 °C, the material exhibits narrow temperature window and can oxidize SO₂ to SO₃ [2]. Due to these operating problems, alternative materials have been studied over the last three decades. Nowadays, most of the attention is focused on the application of modified zeolites as the substitutes of V₂O₅-TiO₂ [3]. These aluminosilicate materials own their promising catalytic features to high acidity, considerable specific surface area, thermal stability of the structure up to 800 °C and well-defined pore system [3,5]. Although some zeolite-based catalysts of NH₃-SCR have been already implemented, there is still no agreement on the issue which group of these materials – natural or synthetic are more preferable for industrial utilization.

In consideration of the aforementioned, the presented research was focused on the comparison of the catalytic performance of iron-modified natural clinoptilolite and microporous layered MCM-22 in NO_x reduction with NH₃. The results of NH₃-SCR catalytic tests performed over the catalysts indicated that raw clinoptilolite exhibits significantly higher activity than non-modified MCM-22. It is probably due to the presence of catalytically active species in the parent natural zeolite. Moreover, the difference in NO conversion between the zeolites was correlated with the temperature range of the reaction. MCM-22 exhibited higher activity below 300 °C and clinoptilolite above this value. The effect was ascribed to the specific speciation of iron on the materials, determined by UV-vis analysis. The concentration of N₂O in the flue gas was below 50 ppm for both catalysts, which points on their high selectivity. Additionally, in the opposite to Fe-modified MCM-22, the amount of by-product was gradually increasing for Fe-modified natural zeolite.

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Dynamer-liposome dynamic system for drug delivery

OC44

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Para-coumaric acid (*p*-CA) is a hydroxycinnamic acid known for its biological antioxidant activities [1]. Low water solubility of *p*-CA limits its absorption and bioavailability. Nanoscale delivery vehicles are considered as efficient platform to increase solubility, and improve therapeutic action of this model acidic drug. Liposomes are biocompatible vesicles able to entrap hydrophobic and hydrophilic pharmaceutical agents [2]. Dynamic polymers - Dynamers are synthesized *via* reversible covalent bonds between the monomers [3]. Dynamically cross-linked networks were grown around liposomes leading to a dynamer-liposome conjugates for drug delivery [4]. In our work, the encapsulation of *p*-CA was performed using egg phosphatidylcholine (EPC) liposomes combined with poly(amidoamine) PAMAM G1 dendrimer and 1,3,5- Benzene tricarboxaldehyde (BTA), poly(ethyleneglycol)bis(3-aminopropyl) terminated (PEG) and stearylamine (SA) for dynamer components. The design of this system was proceeded by simple mixing of EPC liposomes with BTA/PEG/SA (1:1.5:0.5 molar ratio) dynamer or EPC:G1 liposome with BTA/PEG (1:1 molar ratio) dynamer at different concentrations. The analysis of dynamic light scattering (DLS) and scanning electron microscopy (SEM) suggested that dynamers and liposomes were connected forming larger conjugates. The water solubility of *p*-CA (0.64 mg/mL) was increased in presence of conventional liposomes (1.29 mg/mL), and more significantly in presence of BTA/PEG dynamer (3.43 mg/mL). Dynamer-liposome system improved the solubility of *p*-CA, linearly with the concentration of dynamers, compared to conventional liposomes. Furthermore, the *in vitro* release of *p*-CA from conventional liposomes was fast. However, in dynamer-liposome system, the release was slightly delayed (80% of released *p*-CA from dynamer-liposome system versus 100% of *p*-CA from liposome in three hours).

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Design of mesoporous SiC membranes from polymeric precursors for water filtration

OC45

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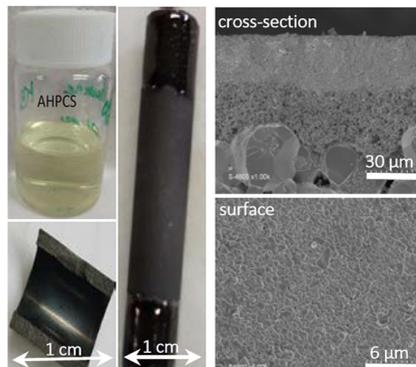


The fabrication of non-oxide ceramic membranes has been intensively studied in the past 20 years, due to the huge potential of these materials for both liquid-phase and gas phase applications. Silicon carbide (SiC) membranes are particularly attractive because of their high thermal and chemical stability [1] (adapted in harsh environment), but also their specific surface properties (limiting fouling phenomena). It has namely been found that macroporous SiC membranes were capable of removing oil, grease and total suspended solids from kitchen waste water [2]. Various strategies, synthesis methods and precursors have been used to fabricate such SiC membranes. A huge challenge relies on the control of their microstructure and more specifically on the development of mesoporous SiC membrane top-layers. In this frame the present work focused on the so-called preceramic polymer route, where polymeric precursors can be converted to SiC by pyrolysis at high temperature ($> 1000^{\circ}\text{C}$) in Ar atmosphere.

We have shown recently that a mixture of allylhydridopolycarbosilane (AHPCS) with a specific pore former (polystyrene-block-polybutadiene-block-polystyrene) could result in mesoporous SiC with a high specific surface area, even after a thermal treatment at 1900°C [3]. In the present work, we aim at coating commercial α -alumina tubular membrane supports with mesoporous SiC originating from AHPCS pyrolysis.

For reaching this objective, we performed a set of assays, involving different formulations of the impregnation solution. We also studied the possibility of using an additional carbon coating of the alumina support in order to change *i)* the surface interaction between the substrate and the SiC polymeric precursor, *ii)* limit infiltration and *iii)* create a barrier preventing the diffusion of elements coming from the alumina substrate into the SiC top-layer during the pyrolysis.

In this communication, I will present the multi-step design of the composite alumina/carbon/silicon carbide membranes, and I will provide a detailed characterization of these materials involving electron microscopy, spectroscopies, and gas adsorption measurements.



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What news on the plutonium-calmodulin variants interaction at molecular scale?

OC46

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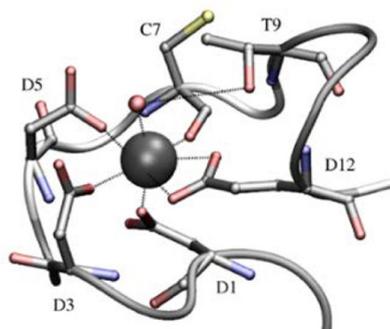
Plutonium is an actinide of major societal relevance due to its large stock worldwide and its key role in the cleanup challenges of legacy nuclear sites. Although its physiological impact has been widely investigated, understanding its interactions with biological molecules remains limited. The knowledge relative to actinide transportation mechanism, and in particular, the direct interaction of Pu at the molecular scale with proteins is still unclear. Recent publications have pointed that Pu interaction with transferrin or ferritin [1], an iron carrier of blood, could be at the origin of its internalization in cells [2] and that calcium-binding proteins are possible Pu targets [3].

This work aims at investigating the interactions between actinide elements, and more specifically plutonium, and biological molecules.[4,6] Calcium-binding EF-hand protein motifs of the calmodulin N-terminal domain, which contains seven coordination sites were chosen for this study. Calmodulin is an important protein expressed in all eukaryotic cells and is involved in a large number of signal transduction pathways.

In vivo, plutonium is mainly present at oxidation state +IV, and at this oxidation state, plutonium is a very high hydrolyses propensity. In this work, we will focus on the interaction of the plutonium (IV)

with two variants of the calmodulin. CaM-WT, which is the wild type calmodulin, and CaME variant in which one threonine is replaced by one glutamate, thus increasing the number of hard donor carboxylate ligands in the binding site. Different routes taking into account the constraints due to the hydrolysis of plutonium (IV) at physiological pH have been used and will be discussed.

The interactions between Pu and calmodulin ligand were then characterized using visible and X-ray absorption spectroscopies and ESI-MS and showed the formation of a complex Pu-Calmodulin for both CaM-E and CaM-WT, close to physiological conditions.



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Enhanced aminolysis of cyclic carbonates by β -hydroxyamines for the production of fully biobased polyhydroxyurethanes

OC47

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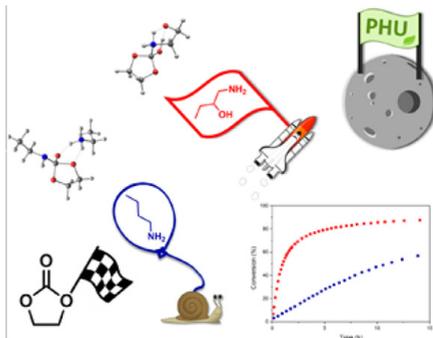


Polyurethanes (PUs), ranking 6th among all polymers based on annual worldwide production, are commonplace in everyday life as foams, coatings, adhesives, elastomers, insulation, composites, and so forth. They are present in a wide range of applications due to the numerous industrially available polyols, which allow to cover a large panel of properties.

However, their synthesis requires the use of isocyanates, known to be harmful for human health and for the environment.[1] In order to limit the use of isocyanates, the development of isocyanate-free PUs has emerged over the last decade and has gained increasing attention in both the academic and industrial communities. Hence, the aminolysis of 5-membered cyclic carbonates, which yields polyhydroxyurethanes (PHUs), is nowadays the most promising and described route to non-isocyanate polyurethanes (NIPUs).[2] This route has the advantage that these carbonates are easily obtained by the carbonation of commercial epoxides. Moreover, the valorization of CO₂ as a cheap, renewable and non-toxic resource makes this pathway the least toxic and most eco-friendly route to PHUs.[3] However, 5-membered cyclic carbonates suffer from lower reactivity compared to isocyanates or larger cyclic carbonates.

Therefore, the aminolysis of cyclic carbonates has been thoroughly investigated in order to understand and optimize the ring opening reaction.[4]

In this study, [5] we highlighted the higher reactivity of β -hydroxyamines toward cyclic carbonate in comparison to classical alkylamines through the determination of their reaction rate constants. The key role of the β -OH substituent in the aminolysis was enlighten by a DFT investigation. In addition to their higher reactivity, biobased β -hydroxyamines were easily synthesized by a one-step process and used for the synthesis of fully biobased PHU thermosets. The higher reactivity of β -hydroxyamines was also confirmed in the thermoset synthesis, the thermal and thermo-mechanical properties of PHUs were then compared.



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Synthesis, functionalization and 3D printing of bioceramics for bone engineering

OC48

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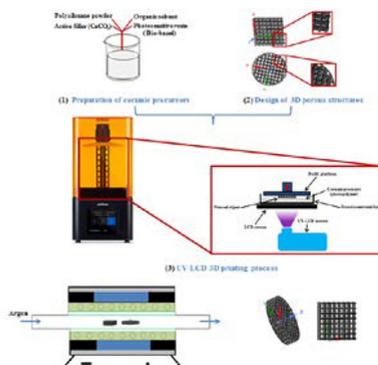
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Bioceramics, widely used for bone engineering due to their biocompatibility and tunable properties, generally display poor antibacterial activity. Infection at the site of implantation can cause failure in bone healing process; therefore, developing antibacterial bioceramics with good mechanical and microstructural properties is required. Silicate-based bioceramics have excellent bioactivity and are considered promising materials for bone regeneration; however, their synthesis and design in complex geometric forms using conventional techniques is still difficult [1,2,3,4,5]. The design of scaffolds for

tissue engineering with the mechanical and microstructural properties required to promoting cell attachment, growth and new tissue formation is one of the major challenges facing researchers and physicians in the field. An important class of materials for bone engineering includes bioceramics and bioactive glasses [6]. Their main disadvantage is their low strength and high brittleness under applied loads. These limitations are exacerbated by the fact that scaffolds must be very porous and stable. In response to these challenges, several solutions are being explored to improve the structural integrity and strength of bioceramics. The Polymer-Derived Ceramics (PDCs) route is one of the most advantageous

approaches in the manufacture of bioceramics due to the ability to control both synthesis and shaping. In this work, customized 3D β - Ca_2SiO_4 structures were fabricated by combining the PDCs route and Stereolithography-3D printing. β - Ca_2SiO_4 scaffolds have been successfully manufactured starting from i) commercial silicone polymer and inorganic oxide fillers mixed with a biobased photosensitive resin and ii) a "home-made" photosensitive preceramic polysilsesquioxane polymer. After pyrolysis, the scaffolds were functionalized by silver nanoparticles uniformly dispersed on graphene oxide in order to assess their antibacterial activity. XPS and TEM analysis along with EELS confirmed the formation of silver nanoparticles throughout the graphene oxide with average particle diameter of 30nm. The antibacterial activity was successfully demonstrated on *Escherichia coli* with a better performance for the "home-made" photosensitive polymer. Due to their interconnected porosity, mechanical and antibacterial properties, these scaffolds would be promising candidates for bone tissue engineering.



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Polyacid-functionalized mesoporous materials: synthesis and evaluation of the performances in heterogeneous catalysis

OC49

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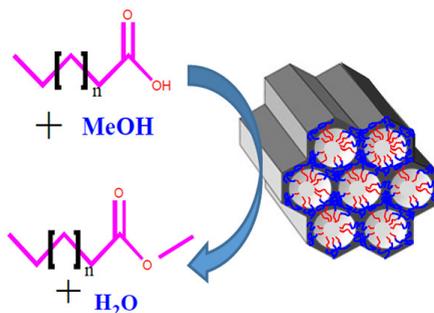


Polymer-functionalized mesoporous silica materials combine the textural properties of mesoporous materials and the chemical properties of polymers. These two features make them excellent candidates for applications in catalysis, adsorption for environmental remediation and drug delivery systems. The synthesis of such hybrid materials is limited by the functionalization step: a high density of polymers and a homogeneous distribution of this polymer within the pores remain difficult to reconcile [1]. Our research intends to synthesize and study the catalytic properties of polymer-functionalized mesoporous silica materials prepared using an innovative and versatile process based on polyion complex (PIC) micelles, which overcome the issues of density and homogeneity of functionalization [2,3].

A system of two hydrophilic polymers is used for the PIC micelle formation through electrostatic interaction, one is a double-hydrophilic block copolymer (DHBC) named poly(ethylene oxide) polyacrylate – poly(styrene sulfonate) (PAPEO-*b*-PSS) and the second is an oppositely charged polyamine (oligochitosan). A sol-gel process allows the PAPEO chains to be anchored in the silica. The polyamines are removed from the structure by pH stimulation, thus revealing the porosity and the acidic functions. Analysis

confirmed that no polyamine remains in the material after the synthesis and that it possesses a density of functions around 0.6 mmol of acidic group per gram of material. The functions are homogeneously distributed, as proved by the highly ordered 2D hexagonal structure and 10nm pores of the material.

Then the materials have been tested as catalysts in the esterification of fatty acids by methanol. This reaction has been chosen because it appears to be a good starting point to study the catalytic activity of the material, corroborated by the number of publications on this reaction for other sulfonic acid functionalized silicas. In our work the reaction presents a conversion around 20%-30% for the esterification of palmitic acid by methanol and 20% for caprylic acid. The results confirmed that the material can be used as a catalyst, however further analysis has to be done to fully comprehend the behavior of the materials in catalysis.



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In vitro and *in vivo* evaluation of antioxidant formulations to treat Macular Degeneration

OC50

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Age-related Macular Degeneration (AMD) is a neurodegenerative pathology affecting photoreceptor cells through the production of a cytotoxic retinoid (A2E) related to lipofuscin accumulation. This mechanism is also involved in inherited macular dystrophy, such as Stargardt's disease, through a double carbonyl and oxidative stress [1].

In this context, Dr. C. Crauste's team developed lipophenolic derivatives able to act against Carbonyl and Oxidative Stress (COS) in order to limit the degeneration of the photoreceptors of the macula [2,3] (LiPoPheRet ANR-18-CE18-0017). This study aim to investigate the development of an oral formulation to improve the comfort of the patients (instead of parenteral injection).

First, the lead molecule "Phloro-IP-DHA" classified as BCS class IV was evaluated and showed promising results *in vivo* after IV administration on Abca4KO mice (Dr. P. Brabet). Then, we decided to develop original formulations to improve its bioavailability after oral administration (Dr. S. Begu). SNEDDS: self-emulsifying nanosized systems were selected and evaluated *in vitro* in terms of size distribution, loading rate, impact of dilution and drug stability. SNEDDS are a mixture of oil, surfactant and co-surfactant that form nano-emulsions upon contact with gastrointestinal fluid. These studies showed the formation nano-emulsions with a size of 60nm from "Phloro-IP-DHA" loaded SNEDDS (SNEDDS-IP-DHA) at 30mg/mL (drug loading = 2.93%). These nano-emulsions were stable in gastric medium and robust to dilution. To prove the effectiveness of our formulation and our molecule, we conducted *in vivo* pharmacokinetics and efficacy tests on the same mouse model used for IV administration. The oral bioavailability with SNEDDS-IP-DHA was increased compared to the molecule solubilized in soybean oil alone. SNEDDS-IP-DHA protected almost all the photoreceptors of Abca4KO mice after acute light-induced retinal degeneration. At the same time, analogs molecules were synthesized in order to obtain a Backup Lead with optimized anti COS activity. Preliminary tests on ARPE-19 cells (efficacy and toxicity) allowed us to select a candidate molecule. IV formulations were developed and evaluated on Abca4KO mice. These tests proved the potential of our new molecule "Quercetin-IP-DHA". In the futur, this molecule could be developed for an oral administration in order to meet the specifications of our study.

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Polymer assisted MOF synthesis and membrane preparation

OC51

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UiO- MOF is a large family of MOFs based on zirconium cluster and carboxylic acid that have excellent chemical and thermal stability, tolerance to linkers of different length and functionalities, making them a good candidate for various different applications [1]. However, difficulties of processing the polycrystalline powder of UiOs (and in general MOFs) limit their application in many fields such as membrane separation. Here, we report for the first time the synthesis the UiO-66 in the presence of well-defined cross-linked poly methacrylic acid-*b*- poly methylmethacrylate (PMAA-*b*-PMMA) nanoparticles prepared *via* Reversible Addition-Fragmentation Chain-transfer Polymerization controlled Polymerization Induced Self-Assembly (RAFT-PISA) [2]. The PMAA-*b*-PMMA nanoparticles with multi carboxylic acid groups on their surface, well-defined in shape and size act as both a macro- surfactant and a multivalent connecting agent for the synthesis of the crystalline MOF structure. The resulting UiO-polymer hybrid materials in form of stabilized suspension are high crystalline, porous and with enhanced processability. Then thin film membranes were prepared by simply vacuum filtrating the UiO-polymer suspension on Nylon supports. This membrane can reach to 93.4% rejection of dye (Nickel(II) phthalocyanine-tetrasulfonic acid tetrasodium salt) with a permeability around 20 L·m⁻²·h⁻¹·bar⁻¹. This kind of new synthesis approach could furthermore be universally applied to the other kind of carboxylic acid linker containing MOF synthesis in order to prepared MOF-polymer hybrid materials that facilitate MOF applications in different fields.

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From high-throughput computational screening to experimental validation for siloxane adsorption in MOFs

OC52

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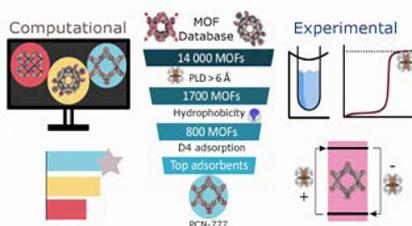
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Octamethylcyclotetrasiloxane (commonly named D4) is one of the most representative volatile methylsiloxanes (VMS) contaminants in biogas streams.[1] Conventional adsorbents such as activated carbons, silicas, and zeolites have been considered for D4 capture [2], however so far, they have not reached the three key criteria together, i.e. high uptake, good selectivity vs. water, and easy regeneration. MOFs (metal-organic frameworks) appear as promising alternative adsorbents due to their highly porous structures, and tailorable chemical and physical properties, but only a very few studies have envisaged their uses for the adsorption of this target molecule. [3,4]

Herein, high-throughput molecular simulations were performed to screen the recent Computation-Ready Experimental (CoRE) MOF database for D4 capture. We selected the hydrophobic MOFs whose pore limiting diameters larger than 6.0 Å to accommodate this relatively bulky molecule. A Zr-MOF was identified as a good candidate in terms of D4 uptake and affinity and this guided the experimental effort towards the synthesis of this sample and adsorption testing. This mesoporous MOF was demonstrated to have a record D4 uptake of 1.8 g.g⁻¹ which is almost twice higher than the performance of the benchmark Cr-based MIL-101 (MIL for Material Institute Lavoisier). Remarkably, this MOF shows a very good cyclability combined with an easy regeneration. We further investigated the adsorption mechanism at the origin of this spectacular performance. This hybrid computational-experimental approach will guide further development of MOFs for the capture of other molecules of this family of VMS.



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Chemical modification impact of graphene or graphite in conductive nanocomposite morphology control

OC53

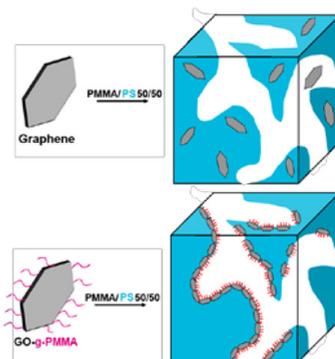
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Carbon fillers are used for nanocomposite application in order to improve mechanical, thermal and electrical properties of polymers [1,2,3]. The last decade, graphene attracted much attention thanks to its 2D structure, high aspect ratio and high surface area. These intrinsic properties made it one of the most promising filler for the development of high added-value polymer nanocomposites. However, as graphene nanoparticles are difficult to disperse in polymer matrices, they must be incorporated in high amounts in order to create a percolation network and to obtain high electrical conductivities. Chemical modification is one of the solutions to improve the dispersion of graphene. Moreover, by controlling the graphene chemical modification to it is possible to orient its localization in an immiscible polymer blend. The present study is focusing first on the chemical modification influence of graphene and graphite on their structure (exfoliation, new covalent bonds). TGA, FTIR and Py-GC/MS characterization proved the chemical modification. XRD showed the structure modification with the intercalation of oxygenated groups and confirmed the exfoliation. Raman spectroscopy revealed high defect concentration due to the strong oxidation and formation of sp^3 carbon. Then, these modified graphene and graphite were dispersed in a co-continuous PMMA/PS polymer blend. Due to the immiscibility of PMMA and PS polymers, an interface is formed during the melt blending. The aim is to allow the localization of the graphene platelets at the continuous interface by their surface modification. By placing graphene platelets at the interface, the percolation threshold is decreased [4]. Moreover, this localization at the interface is facilitated by the high exfoliation degree that tends to improve the flexibility of graphene particles. To reach the interface localization, graphene was first oxidized and then functionalized with a copolymer of methyl methacrylate and hydroxyethyl methacrylate (P(MMA-co-HEMA)). Then, functionalized graphene was dispersed in the PS matrix by solvent casting. This master batch was mixed by melt blending with the PMMA matrix. Due to the better affinity with PMMA, the functionalized graphene migrates to the interface during the melt process. AFM, SEM allowed to identify the localization of the functionalized graphene and graphite in polymer blends. Finally, a performant electrical material can be elaborated with lower amounts of graphene for uses in energy storage or aeronautic.



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Design of advanced photocatalytic materials by Atomic Layer Deposition (ALD)

OC54

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Due to the increasing contamination of our natural water resources by a wide range of organic micropollutant (OMPs), there is a need for developing new energy-efficient advanced oxidation processes for the treatment of water contaminated by such refractory pollutants.

Photocatalysis has attracted much attention, due to its ability to degrade toxic organic compounds in wastewater into environmental friendly compounds such as CO₂ and water [1].

Among the various photocatalytic materials, titanium dioxide (TiO₂) has been widely used due to its high photocatalytic efficiency, high stability and low toxicity. However, fast charge recombination and the narrow absorption range in the UV spectrum; limit its photocatalytic efficiency under visible-light irradiation [2].

In this work TiO₂ nanofibers were synthesized by electrospinning method. In order to improve the photocatalytic activity under visible light, a developed process based on atomic layer deposition (ALD) was used to grow boron nitride (BN) and palladium (Pd) on these fibers. The morphological, structural and optical properties of all fibers were investigated by several characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

The influence of chemical and physical properties on the photocatalytic degradation of acetaminophen has been investigated. The results indicate that acetaminophen is stable and difficult to be photodegraded in the absence of photocatalyst. After 4h of visible light irradiation, acetaminophen has been degraded up to 90% in the presence of TiO₂-BN-Pd nanofibers, compared to only 20% degradation with pure TiO₂.

Based on these promising results, the development of ceramic nanofiltration membranes coated with these highly photocatalytic materials will be investigated. In parallel, a better understanding of the photocatalytic oxidation pathways (based on by-product analysis) coupled with toxicity tests (Vibrio Fisheri, Microtox) will be studied.

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Hydration mechanisms of uranium dioxide (UO_2): new insights from *ab initio* molecular dynamics simulations

OC55

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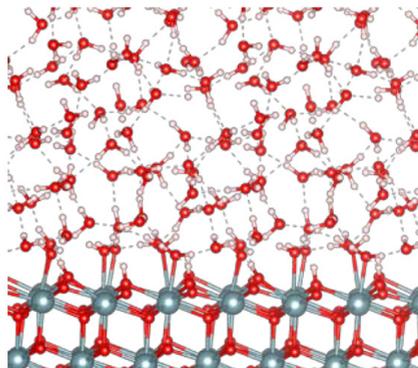
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After their stay in the reactor, spent nuclear fuels (SNF) are still composed of more than 95 wt.% of uranium dioxide (UO_2) and 1 wt.% plutonium dioxide, which constitute valuable secondary resources. In France, the SNF can be reprocessed in order to recover remaining uranium (and plutonium). The head-end step of this process deals with the dissolution of the SNF in hot and concentrated nitric acid, followed by the separation and purification of uranium and plutonium oxides. Besides, one of the potential solutions for long-term isolation of the end-of-life SNF is its direct disposal in deep geological repositories, where

UO_2 surfaces could be in contact with water with various possible physical-chemical conditions. Acquiring a thorough understanding of the stability of UO_2 in various physical-chemical conditions is therefore of paramount interest to (1) assess the long-term behavior of the end-of-life SNF in geological repository conditions and (2) finely tune the UO_2 dissolution stage in the reprocessing of the SNF. Here, for the first time, we employed *ab initio* molecular dynamics simulations to thoroughly characterize the hydration mechanisms of the (111) surface -the main cleavage plane- of UO_2 , and, particularly, the dynamic equilibrium of this surface in presence of pure water. The surface coverage was gradually increased from a single



water molecule to the system where the vacuum above the surface was completely filled with water molecules (see picture). For a single water molecule, the molecular adsorption was significantly favored ($\Delta H_{\text{ads}} = -47.6 \text{ kJ mol}^{-1}$) over the dissociated adsorption ($\Delta H_{\text{ads}} = -13.1 \text{ kJ mol}^{-1}$). However, for two water molecules both introduced in their molecular form, one adsorbed under its molecular form while the second spontaneously dissociated on the surface: the OH^- anion adsorbed on an uranium atom of the surface while the H^+ ion adsorbed on a surface oxygen atom. For higher surface coverages, we systematically observed that a significant part of the water molecules spontaneously dissociated on the surface while ΔH_{ads} tended towards the enthalpy of condensation of water with increasing coverages. When the cell was completely filled with water, about a third of the surface uranium atoms were hydroxylated, which meant that 33% of the water molecules of the monolayer dissociated on the UO_2 (111) surface. A dynamic equilibrium between the bulk of water and the surface was established, with frequent recombination/dissociation of water molecules as well as adsorption/desorption of HO^- , H^+ , or H_2O . This work will serve as a basis for further studies, particularly about the dissolution mechanisms of UO_2 in presence of nitric acid.

Catalyst-free transesterification vitrimers: the power of fluorine to activate bond exchanges

OC56

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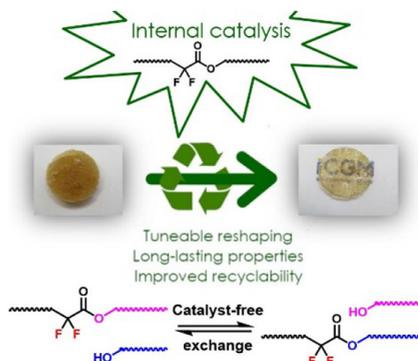
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Vitrimers are a class of polymers bridging the gap between resistant 3D thermosets and recyclable linear thermoplastics.[1]

Their crosslinked network similar to thermosets allows exceptional resistance to solvents, while the embedded exchangeable bonds allows their recyclability. Since the first polyester vitrimer described by Leibler et al. in 2011,[2] many exchangeable bonds were investigated. Recently, strategies such as activation by inductive effects or neighboring group participation [3-5] were implemented on exchangeable bonds in such materials to tune the rate of exchanges and the materials recyclability without requiring catalysts.

We unveil here a novel activating group based on alpha-difluoro esters. Fluorine features exceptional properties, in particular a strong electronegativity, which activates reactions such as transesterification.[6,7] When implemented in polyester vitrimers, this group allows to synthesize highly crosslinked materials with satisfying reshaping abilities without any metallic or organic catalyst usually needed for such vitrimers. This strategy avoids the risk of catalyst leaching and slows down the premature ageing upon recycling process. Thereby the synthesized material combines durability, recyclability and are catalyst-free. This discovery is one step further on the way towards greener recyclable plastics.



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Designed catalytic nanostructures for the biomass electro-reforming in membrane electrolyzers

OC57

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A question stemming from electrochemical converters is how the *next generation water splitter could help renewables power the globe* through the so-called H_2 -fuelled fuel cells, satisfying both criteria of “decentralized and decarbonized electricity”. It is accepted as a *fait accompli* that this simple molecule H_2 is a cornerstone in the energy transition, acting as an energy carrier. Indeed, the overall operating reaction of this elegant power source indicates that the only formed product is H_2O , which could in return be split to produce the reactants ($2H_2 + O_2 = 2H_2O$). It is noteworthy to note that H_2 is overwhelmingly employed for the Haber–Bosch process of ammonia synthesis,

Fischer–Tropsch process of hydrocarbon synthesis and metal refining. Conclusively, H_2 serving as a CO_2 -free fuel is also a staple of the chemical industry. However, precisely how H_2 could be synthesized in a cheap and sustainable way remains a puzzle for scientists.

Either H_2 is produced by CO_2 -polluting routes of thermal decomposition of fossil fuels or a significant portion of the energy required for the operation is consumed by the accompanying reaction at the positive electrode in electrolyzers. So, the emerged question in membrane electrolyzers is *how the large biomass could offer a renewable alternative to fossil sources?* Given their low oxidation potential compared to H_2O , organics at the anode compartment greatly allow saving nearly 50% of the energy input. Even more interesting, a tight control over selectivity will enable the genuinely sustainable production of high value-added chemicals from renewable sources in addition to H_2 (paired electrosynthesis). However, designing a material to be used as a catalyst which bridges the activity and selectivity trends in organic electrosynthesis is a challenge for both theoreticians and experimentalists in electrocatalysis. Our research group is engaged in the performance-by-design approach to develop nanostructured electrocatalysts capable of efficient electro-reforming of biomass-based compounds in order to power the transition to a sustainable circular economy.[1,2] We will present our last outcomes on the electro-reforming of biomass derivatives (Figure 1), targeting a cogeneration process to decrease the overall cost of carbon-free pathway of H_2 production. Given the current great interest for the development of electrochemical membrane reactors to produce green H_2 from water, transform CO_2 into platform molecules and synthesis NH_3 by using N_2 , our developed materials can also stand for the large diversity of the bio-energy production of value-added fuels or chemicals.[3,4]

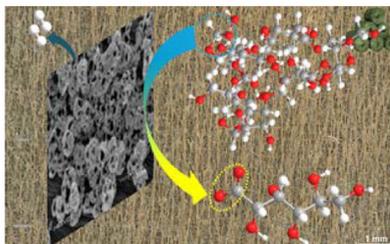


Figure 1: Sketch of selective biomass electro-conversion to valuable organic molecules and H_2 at alloys of Au-Ag nanocages in membrane electrolyzer.

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Synthetic methodologies and study of thermosetting resins obtained from biobased and/or non-toxic compounds for the recovery of critical metals

OC58

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Phenolic resins are remarkable thermosetting polymers owing to their thermal and chemical stability, their fire and abrasion resistance, their electrical and thermal isolation properties, and their rigidity. These materials have been widely used for critical metals recovery such as lanthanides, due to their outstanding ion exchange properties in solid-liquid extraction. Furthermore, organic ligands, which act as complexing agents can be introduced in the polymer matrix in order to enhance extraction properties, and selectivity toward metals. However, the synthesis of phenolic resins from hazardous chemicals, specifically formaldehyde and phenol, remains a critical aspect in the development of these polymers. Here in, we report phenolic thermosetting resins, synthesized from bio-based and / or non-toxic compounds for lanthanides extraction. The raw materials used are resorcinol and terephthalaldehyde. The phenolic resins were obtained by a two-step polymerization reaction: firstly, the prepolymerization step was carried out at low temperatures, and then the crosslinking step at 180 °C. The molar ratio of the starting materials was optimized thus, leading to high crosslinked polymers. The resins were characterized by ¹H NMR, IR, TGA and DSC analyses. The as synthesized materials are highly crosslinked and water insoluble, which allows their use in solid-liquid extraction process. The extraction efficiency of the resins toward lanthanides (lanthanum, neodymium, europium, dysprosium and ytterbium) was evaluated in acidic media. The effects of pH of the feed solution, and resin concentration on the sorption properties (efficiency, kinetic, loading capacity) were investigated in the solid-liquid experiments. The results display a good efficiency and sorption capacity for such materials, which reached a capacity of 50 mg.g⁻¹ at pH = 4, with fast kinetics (all the lanthanides can be extracted in 2 hours). The back-extraction showed that the extracted metals can be recovered, and the solid phase can be reused. These promising results for such formaldehyde free resins are comparable to those obtained with conventional phenol formaldehyde resins.

Determination of porous surfaces and volumes in mesoporous zeolites for catalytic valorization of methylmercaptan

OC59

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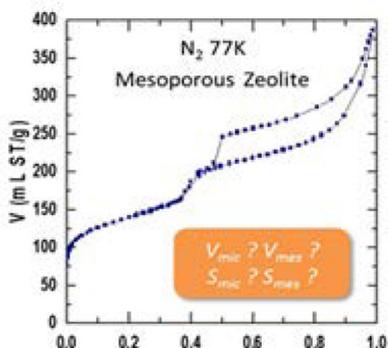
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Catalytic processes enable a large range of industrial reactions by lowering activation energies. Furthermore, for environment purpose and for the on-going energy transition new natural and eventually waste feedstocks are envisaged to replace manufactured reactants. Recently, it was demonstrated that methylmercaptan (CH_3SH), an impurity present in natural gas, can replace methanol in the catalytic conversion of toluene into p-xylene [1], a product in high demand for the production of polyethylene terephthalate (PET). The tested catalyst was a commercial ZSM-5 zeolite [1]. However, a mixture of xylene isomers was obtained due to intraparticle diffusion

limitation in the microporous catalyst. In order to increase diffusion and therefore the selectivity in p-xylene, this project aims at developing the use of hierarchical zeolites for this reaction. Adding mesoporosity to zeolites enhances reactants and products diffusion, increases the accessibility to the active sites, improves catalyst lifetime thanks to the diminution of coke formation and a slower deactivation rate [2-5]. Hierarchical zeolites prepared by "micelle-templating" [2] and presenting a MCM-41-type homogeneous and ordered mesoporosity have shown promising catalytic performances [2-5]. In this study, various hierarchical zeolites (FAU-Y, ZSM-5, MOR, *BEA) were prepared by "micelle-templating". The porosity characterization of such hierarchical materials requires special care. Thanks to mechanical mixtures of FAU-Y and MCM-41, it was demonstrated the usual t-plot method, deduced from N_2 adsorption isotherms at 77 K, underestimates microporous volume (V_{mic}) [6] and overestimates mesoporous surface area (S_{mes}) [7]. Abaci were provided for corrections of t-plot analysis. In this study, the mechanical mixture method was implemented with various commercial acidic zeolites (ZSM-5, MOR, *BEA). The resulting corrected t-plot method was used to access micro- and mesoporous surface areas and volumes of the hierarchical zeolites. The corrected t-plot method for V_{mic} was in good agreement with the benchmark NLDFT Ar 87K method, which does not allow to access surface areas. Hierarchical zeolites with equivalent meso- and microporous volumes or surface areas were identified and ready for further catalytic evaluation in the alkylation of toluene.



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Preparation of well-defined 2D-lenticular aggregates by self-assembly of PNIPAM-*b*-PVDF amphiphilic diblock copolymers in solution

OC60

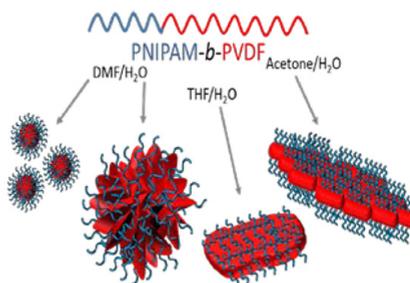
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The development of new materials based on Poly(vinylidene fluoride) (PVDF) is highly attractive as they are employed in high economic impact fields as coatings, electronics, and water filtration.[1,2] Recently, the reversible addition-fragmentation chain transfer (RAFT) polymerization of VDF has been thoroughly investigated, and has been shown to be an efficient method to prepare PVDF with predictable molar mass, narrow molar mass distribution and high end-group fidelity.[3-5] Self-assembly of block copolymers can yield a diverse array of morphologies. The obtained nanostructures are influenced by the polymer structure and block nature. The self-assembly of PVDF block copolymers in solution has only been described recently,[6-11] since well-defined PVDF-containing block copolymers are difficult to synthesize. In this work we report the of PNIPAM-*b*-PVDF (poly(*N*-isopropylacrylamide)-*b*-poly(vinylidene fluoride)) amphiphilic block copolymers (BCPs) *via* RAFT polymerization from PNIPAM macromolecular chain transfer agents (macro-CTAs). PNIPAM was used as it is one of the few hydrophilic polymers soluble in dimethyl carbonate (DMC) and which can be synthesized using a xanthate CTA with relatively good control. The polymerizations were conducted at 73 °C in DMC using two PNIPAM macro-CTAs of different molar masses and targeting various DPs for the PVDF block. The RAFT polymerization of VDF resulted in relatively well-defined BCPs ($\bar{D} \leq 1.50$). These amphiphilic BCPs were able to self-assemble into various morphologies such as spherical, crumpled, lamellar and lenticular 2D aggregates by changing the common solvent or the self-assembly protocol. The size of the aggregates could be controlled by varying the DP of the PVDF block. The polymers were characterized by ¹H and ¹⁹F NMR, SEC, TGA and DSC, and the assembled structures were studied by TEM, SEM and AFM. The thermosensitive behavior of the 2D lenticular aggregates was also examined.



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Polymer-assisted supercritical CO₂ extraction of Pd from supported catalysts: a step toward green recycling of precious metals

OC61

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Precious metals, especially palladium (Pd), have a crucial role in daily life thanks to their use in a wide range of applications from electronics to automotive catalysts. However, important industrial markets like Europe, India and China have not natural resources of palladium. Spent end-of-life supported catalysts are a strategic secondary resource to ensure the future supply of such critical metals (circular economy). Nowadays, pyrometallurgical and hydrometallurgical processes are used for the recovery of the metals from spent catalysts but these methods are high energy demanding and generate large volumes of effluents to be treated. In contrast, SUPERMET project [1] aims at developing a green process to recycle precious metals, in particular palladium (Pd) and platinum (Pt), especially from spent supported catalysts from petrochemistry and automotive catalysts. The technology consists in metal extraction in supercritical CO₂ (scCO₂) thanks to CO₂-philic complexing polymers bringing the insoluble precious metal into the scCO₂ medium (Figure 1). [2]

In this contribution, we will present promising results regarding the polymer-assisted extraction of palladium from aluminosilicate-supported catalysts in supercritical carbon dioxide. We have tested various CO₂-philic polymers bearing different complexing units for the metal extraction experiments. [2,3] For instance, one successful polymer was the poly(4-vinyl pyridine-*grad*-1,1,2,2-tetrahydroperfluorodecylacrylate) gradient copolymer, named P(4VP-*grad*-FDA), which was able to extract up to 73% of palladium from the aluminosilicate support.

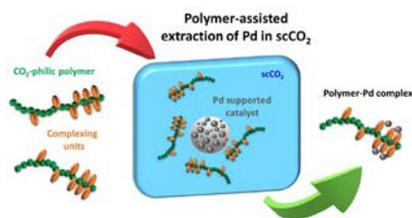


Fig. 1: Polymer-assisted extraction of Pd in supercritical CO₂

[1] <https://supermetproject.eu/>. The authors thank ANR, ADEME, JUELICH/BMBF, and UEFISCDI for financial support of this project in the frame of the ERA-MIN 2 joint call 2017 co-funded by the Horizon 2020 program of the European Union.

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First evidence of size-dependence on structure transition of gold nanoparticles under H₂ by combined *in situ* HRTEM and AIMD simulations

OC62

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Gold nanoparticles (NPs) are known to exhibit promising catalytic performances in many reactions, including catalytic hydrogenation [1]. Many concepts have been proposed to explain the origin of these performances. In particular, the enhancement in activity of Au NPs with size less than 5 nm has been often attributed to the rising fraction of surface atoms and especially those having very low coordination numbers [2,3]. It has been also commonly assumed that Au nanocatalysts are perfect crystals with complete outer surface layers and that no alteration of the coordination of surface atoms occurs during catalytic reaction, which is demonstrated herein as erroneous.

In this presentation, I will present our combined Environmental TEM (ETEM) and *Ab initio* molecular-dynamics (AIMD) simulations study that we performed to examine at the atomic scale the structural dynamics of Au NPs exposed to hydrogen atmospheric pressure. The ETEM observations during H₂ exposure show that while Au NPs larger than ~4 nm remain nearly rigid fcc structures (Fig.1a), smaller ones exhibit drastic and continuous changes in structure symmetry leading to rounded shape NPs (Fig. 1b). The AIMD simulations confer the observed strong atomic flexibility to the high mobility of gold atoms in presence of hydrogen. Unprecedented stable structure of hydrogenated gold surface is identified with bridge-bonded hydrogen-gold crowns decorating a strongly distorted icosahedral-like core (Fig. 1c). This work provides atomic scale insights on gold surface during hydrogenation reactions and suggests the necessity of reinvestigating structure-activity relation and observable factors of gold catalysts through a more realistic picture.

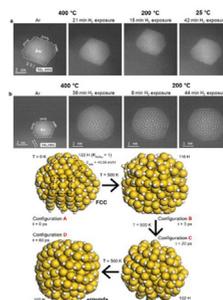


Figure 1: ETEM visualizations of structural evolution of Au NPs in H₂ at atmospheric pressure (a) for Au NPs with size > 3nm b) for Au NPs with size < 3nm. c) AIMD configurations at 500K of modelled gold NP covered by hydrogen

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Understanding the synthesis and reshaping of fluorinated polyester vitrimers: a kinetic study

OC63

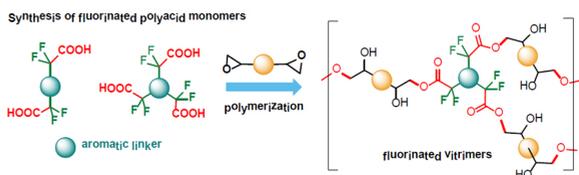
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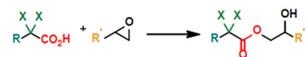


Vitrimers are a new class of polymers that were first introduced by Leibler in the last decade [1]. Such cross-linked polymers are characterized by the dynamic character of their tridimensional network. Indeed, thanks to the introduction of exchangeable chemical bonds, dynamic cross-links can be obtained, which allows for the reshaping, repairing, and recycling of the material [2,3]. This ability is particularly desirable as recyclability is often stated to be the Achilles heel of the related thermosetting polymers. Among the numerous vitrimers that have been described in the literature, polyesters have been given particular attention [2]. Indeed, by reacting polyacids with epoxides, polyesters possessing free alcohol functions are obtained, and the dynamic cross-linking occurs through transesterification reactions of the ester moieties with the free hydroxyl functions. One of the main drawbacks of such vitrimers is the need for catalyst for both the vitrimers synthesis and reshaping. To tackle this issue, we have recently started to investigate the preparation of such polyester vitrimers introducing

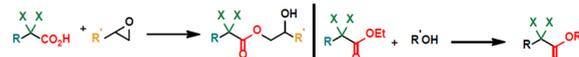


Kinetic studies on the synthesis and reshaping of the vitrimer

Polymer formation (epoxide opening)



Reshaping (transesterification)



positive kinetic effect of fluorine on both the epoxide opening and transesterification reactions

fluorine atoms in the α and β position to the carbonyl function. Interestingly, these vitrimers were found to be formed and recycled in the absence of any sort of catalyst. To better understand the behaviour of these vitrimers, we have carried out a series of kinetic experiment on related monofunctional substrates and we have demonstrated the strong kinetic effect of neighboring fluorine atoms on both the epoxide opening (polymer formation) and transesterification (reshaping) steps.

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Task-specific ionic liquids for the synthesis of functional carbonaceous materials

OC64

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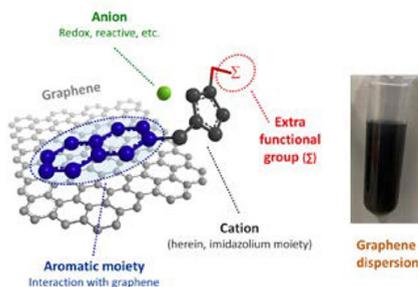


Ionic liquids are liquid salts at room temperature, with melting points less than 100°C, arbitrarily set with reference to the boiling point of water. They often result from an imidazolium cation interacting with an inorganic anion. They are well known for their high ionic conductivity, high charge density and their wide electrochemical window that have favored their use as electrolytes in energy production and storage devices.[1] They are considered as green solvents for their almost zero vapor pressure, non-flammability, high thermal stability, as well as the great possibility of their recycling. Recently, they have shown a promising efficiency in the environmental field especially by their great capacity to adsorb greenhouse gases more precisely carbon dioxide. [2]

We focus our effort on the synthesis of functional carbon materials in ionic liquid medium in order to meet energy and environmental applications. Graphene, the basic entity of graphite, with exceptional properties (remarkable mechanical resistance, high electrical conductivity, optical transparency) was used in electronics, electromagnetism and optics.[3] Its production remains delicate; hence, the interest of our work by using new imidazolium-based ionic liquids bearing aromatic groups to promote the separation and functionalization of the graphene layers constituting graphite through π - π stacking.[4] The exfoliation of this two-dimensional material by these ionic species was studied by sonochemistry or mechanochemistry (ball-milling).

In addition, ionothermal carbonization of biomass (agricultural waste) in presence of ionic liquid is achieved. The effect of the groups carried by the imidazolium cation on the yield of ionochar, on its structure and its porosity is also studied.

The resulting carbon-based materials functionalized by ionic liquids will be investigated in the development of various devices such as high performance electrodes for energy storage and conversion, actuators, gas sensors and we hope they lead to significant progress in energy and environmental protection.



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