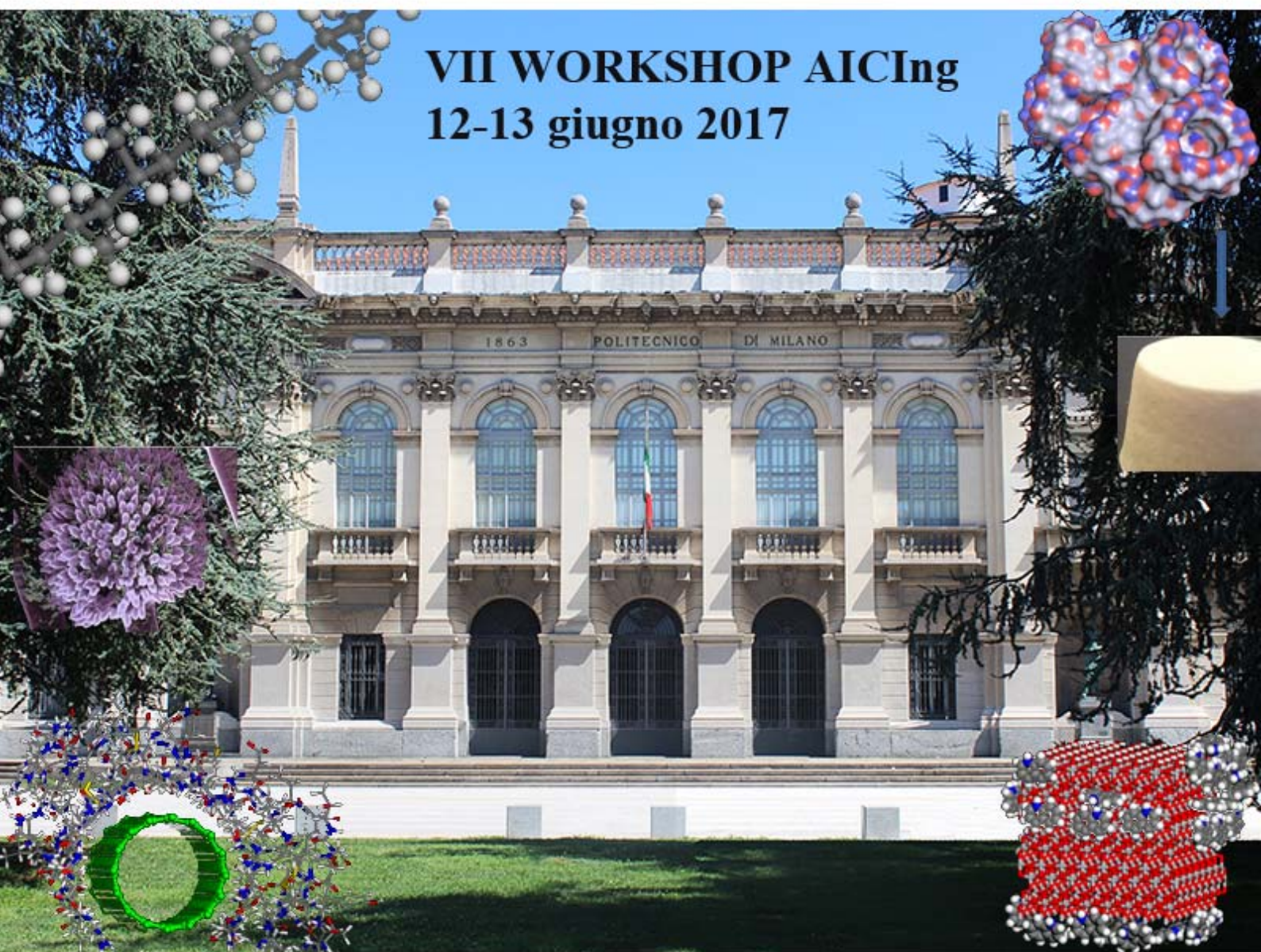




POLITECNICO MILANO 1863

**VII WORKSHOP AICIng
12-13 giugno 2017**



AICIng

Associazione Italiana di Chimica
per Ingegneria

**SMART MATERIALS FOR TECHNOLOGY:
PREPARATION, SELF-ASSEMBLY, CHARACTERIZATION, MODELING**

ATTI DEL CONVEGNO



Associazione Italiana di Chimica
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VII workshop nazionale AICIng

**“SMART MATERIALS FOR TECHNOLOGY:
PREPARATION, SELF-ASSEMBLY,
CHARACTERIZATION, MODELING”**

Milano, 12-13 giugno 2017

**Auditorium del Politecnico di Milano
Viale Romagna, 62**

Programma e libro degli Abstract

EdiSES

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PROGRAMMA SCIENTIFICO workshop AICIng 2017

Lunedì 12 giugno

8:30-9:00	Registrazione presso Auditorium del Politecnico di Milano
9:00-9:20	Saluti di benvenuto: Prof. Maurizio Masi - Direttore del Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta" (<i>Politecnico di Milano</i>) Prof.ssa Chiara Castiglioni - Coordinatore del Dottorato di Ingegneria dei Materiali (<i>Politecnico di Milano</i>) Prof. Alessio Frassoldati - Coordinatore del Dottorato in Chimica Industriale e Ingegneria Chimica (<i>Politecnico di Milano</i>) Prof. Salvatore Failla – Presidente AICIng (<i>Università degli Studi di Catania</i>)
9:20-10:00	Conferenza Plenaria Prof. Paolo Ferruti
Sessione 1: Chairperson Giuseppina Raffaini	
10:00-10:15	Beatrice Berionni Berna: Corrole-phthalocyanine conjugates: when union is strength for optoelectronics
10:15-10:30	Lorena Anna Ditta: Multifunctional nanogels from e-beam irradiation of PVP aqueous solutions, only
10:30-10:45	Emilia Paone: Selective transfer hydrogenolysis of benzyl phenyl ether promoted by Pd/Fe ₃ O ₄ catalyst
10:45-11.:40	Francesco Distanto: Vicinal effect in the Ring Opening Polymerization (ROP) of lactones
11:00-11:30	<i>Coffee Break</i>
Sessione 2: Chairperson Elisa Fasoli	
11:30-11:45	Bianca Gumina: Bio-ethanol production from crystalline cellulose promoted by the heterogeneous PdFe catalyst
11:45-12:00	Arianna Rossetti: Synthesis of Novel Bispidine Ligands and their Coordination Polymers
12:00-12:15	Roberto Sole: Smart Materials for Active Packaging
12:15-12:30	Francesca Baldassarre: Development and prospects of nanostructured smart systems for crop protection

12:30-12:45	Ivan Pietro Oliveri: Synthesis, aggregation properties, and computational investigation on a series of bis(salicylaldiminato)zinc(II) Schiff-base complexes varying the bridging diimine
12:45-13:00	Andrea Savoldelli: Poly-acrolein microspheres functionalized with cobalt corroles for chemical sensor applications
13:00-14:30	<i>Pranzo presso l'Auditorium del Politecnico di Milano</i>
Sessione 3: Chairperson Franca Castiglione	
14:30-14:45	Veronica Ambroggi: Light-triggered release of natural active agents from polymeric nanocapsules
14:45-15:00	Irene Vassalini: Polycarbonate/Carbon Nanotube/TiO ₂ Composite Photoactuators for Chemical Application
15:00-15:15	Vincenzina Barbera: Domino reaction for the controlled functionalization of sp ² carbon allotropes
15:15-15:30	Emanuela Mastronardo: Synthetic strategies for tailoring the performances of Carbon/Mg(OH) ₂ materials for thermochemical heat storage application
15:30-15:45	Mario Branchi: Poly(phenylene sulfide sulfone), polymer electrolyte with improved oxidation stability for redox flow battery applications
15:45-16:15	<i>Coffee Break</i>
Sessione poster: Chairperson Davide Tessaro	
16:15-17:15	Presentazioni Flash su Poster
17:15-18:30	Sessione Poster
20:00	Cena Sociale al "Birrificio Lambrate" – via Golgi, 60

Martedì 13 giugno

Sessione 4: <i>Chairperson</i> Giancarlo Terraneo	
9:00-9:15	Luca Catalano: Engineering Crystalline Supramolecular Rotors via Halogen Bonding
9:15-9:30	Matteo Busato: Structural and Thermodynamic Properties of Transition Metal Ions in Room Temperature Ionic Liquids (RTILs)
9:30-9:45	Andrea Fiorati: Cellulose based materials: from environmental application to controlled drug release
9:45-10:00	Gabriele Tarquini: Lithium polysulfide catholyte for lithium–sulfur batteries
10:00-10:15	Roberto Grisorio: Molecular Tailoring of Phenothiazine-Based Hole-Transporting Materials for High-Performing Perovskite Solar Cells
10:15-10:30	Renato Pelosato: Iron doping and Ba deficiency in $\text{NdBaCo}_2\text{O}_{5+\delta}$ Cathodes for IT-SOFCs
10:30-11:00	<i>Coffee Break</i>
Sessione 5 : <i>Chairperson</i> Lucio Melone	
11:00-11:15	Laura Piperno: Study of two different Artificial Pinning strategies in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films deposited by Metal Organic Decomposition method
11:15-11:30	Giuseppina Luciani: Ceramic templated melanin nanostructures: a novel synthesis approach to bio-functional hybrid materials
11:30-11:45	Flavia Bollino: Chemical characterization of organic-inorganic hybrids synthesized via sol gel for the biomedical field
11:45-12:00	Alessandra Vitale: Photocured siloxane polymers for genomic microfluidic applications
12:00-12:30	Premiazioni e chiusura lavori

SESSIONE POSTER

- **FP1** **Bernardi, Andrea** Master curves for the mechanical reinforcement of diene elastomers with sp^2 carbon allotropes
- **FP2** **Vergaro, Viviana** A preliminary in vivo evaluation of $CaCO_3$ nanocrystals for drug delivery
- **FP3** **Maiolo, Daniele** Self-Assembled Bio-Reducible Hybrid Supraparticles
- **FP4** **Ragusa, Andrea** Engineered NanoDrugs for the Treatment of Parkinson Disease
- **FP5** **Petroselli, Manuel** Aerobic Oxidation catalyzed by N-hydroxy compounds: New frontiers in industrial and biological applications
- **FP6** **Gurian, Elisa** New solid SERS substrates in bioanalytics
- **FP7** **Trovato, Valentina** Humidity/temperature sensing cotton fabric based on MWCNTs hybrid coating
- **FP8** **Rainer, Alberto** Engineering functional skeletal muscle networks by tailoring matrix stiffness and geometrical confinement
- **P09** **Allegretti, Chiara** Lignin-based nanofillers for bio-based thermoplastic polymer nanocomposites
- **P10** **Bursi, Elena** Investigations on activating solutions from waste and by-products treatment for geopolymerization
- **P11** **Casalegno, Mosè** Charge separation at organic photovoltaic interfaces: a coarse-grained quantum chemical view
- **P12** **Chronopoulou, Laura** Biosynthesis of injectable peptide hydrogels for biotechnological applications
- **P13** **Crotti, Michele** Multienzymatic and Stereoselective preparation of 2,3-Disubstituted Tetrahydrofurans: The Roasted Meat Aroma Synthesis
- **P14** **Curcio, Efrem** Membrane-based crystallization of biomolecules
- **P15** **Del Sole, Roberta** Molecularly Imprinted Solid Phase Extraction as a novel approach for radiopharmaceutical products purification
- **P16** **Faura Munoz, Georgina** Synthesis of $Fe_3O_4@SiO_2$ -DFO Nanoparticles for Lanthanide(III) recovery
- **P17** **Leonardi, Gabriella** Synthesis of pyrrole derivatives of serinol for functionalization of carbon allotropes

- P18 **Pandolfi**, Fabiana BMIm Acetate as Carbene Source: an Electrochemical Evidence
- P19 **Pennetta**, Chiara Amino- and guanidinoglycoside based vectors for cell transfection
- P20 **Pugliese**, Andrea Anisotropic diffusion in PEO-LiTFSI-Pyr₁₄TFSI ternary systems: ¹H microimaging NMR study
- P21 **Rossi**, Bianca Aerogels of enzymatically oxidized galactomannans: versatile delivery systems of antimicrobial compounds and enzymes
- P22 **Suranna**, Gian Paolo Truxene-based Hole Transporting Materials for Perovskite Solar Cells: Direct vs Inverted Configuration Devices
- P23 **Tentori**, Francesca Calcium alginate: a powerful tool in technological upgrade for biocatalytic reactions. Immobilization of *Acetobacter aceti* in 1,3-diols oxidation
- P24 **Vitiello**, Giuseppe On the morphological, structural and charge transfer properties of F-doped ZnO: a spectroscopic investigation

COMUNICAZIONI ORALI

Polyamidoamines: hystorical background, properties, recent developments and perspectives

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Polyamidoamines (PAAs) are a family of synthetic polymers obtained by the stepwise polyaddition of prim- or sec-amines to bisacrylamides. The reaction occurs in water at room temperature and $\text{pH} \geq 8$, with neither added catalysts nor organic solvents. Most PAAs are water-soluble or at least water swellable. PAAs are degradable in aqueous media and many of them are remarkably biocompatible. Nearly all conceivable bisacrylamides and prim- or sec-amines can be employed as monomers endowing PAAs of a structural versatility nearly unique among stepwise polyaddition polymers, which makes it easy to prepare purpose-tailored samples for specific applications.

The first intimation of a linear high polymer prepared by polyaddition of sec-diamines with bisacrylamides is in a patent application dating back to 1956 that was no further developed.¹ Extensive studies on this type of stepwise polyaddition were independently started in the sixties at the “Istituto di Chimica Industriale” of the Polytechnic of Milan. The resultant polymers, PAAs, were first object of several papers on “La Chimica e l’Industria (Milan).”² These preliminary papers were then collectively reviewed in 1970.³ Slightly afterwards, some PAAs were also independently reported elsewhere.⁴ Chemistry, properties and applications of PAAs were subsequently reviewed at intervals.⁵⁻⁸ It was soon realized that sterically hindered amines reacted sluggishly, but more recently some salts of earth alkali metals, as for instance calcium chloride, proved to exert a catalytic activity.⁹ In their presence, the reaction rate rose to acceptable levels. The structural versatility of PAAs was exploited in such disparate fields as water pollutant scavengers, transfection promoters, diagnostic probe carriers, antiviral and antimalarial agents, scaffolds for cell culturing and tissue regeneration. The most important results obtained in these fields will be presented.

Finally, a very recent development of PAA chemistry involves the use of chiral α -aminoacids as monomers. Both modeling studies and spectroscopic determinations suggest that the resultant PAAs, besides being chiral, acquire pH-dependent ordered conformations in aqueous solution notwithstanding the chiral centers of their repeating units do not pertain to the polymer chain, but are present as side-substituents.

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Corrole-phthalocyanine conjugates: when union is strength for optoelectronics

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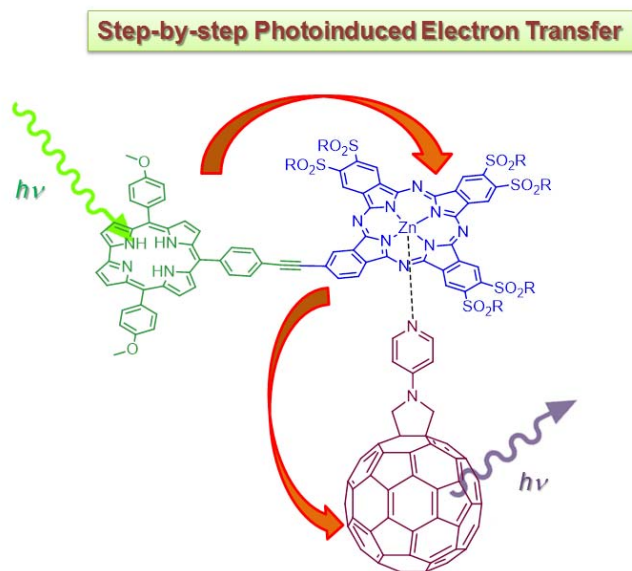
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Among the chromophores that have been used as molecular components in artificial photosynthetic systems, phthalocyanines (Pcs) and corroles (Corr) enjoy a privileged position because of their unique physico-chemical properties which render these macrocycles valuable building blocks in materials science.^[1-3]

In the present study, we have synthesized a donor-acceptor Corrole-Phthalocyanine dyad *via* a Sonogashira cross coupling reaction. The presence of several methoxy groups on the corrole framework is expected to improve the electron-donor properties of such a macrocycle thus enhancing the electron transfer to the linked zinc phthalocyanine, bearing electron-withdrawing groups. Furthermore, our ZnPc was allowed to interact, via a non-covalent approach, with a conveniently functionalized fullerene C₆₀, by means of metal-ligand axial coordination to form the donor-acceptor conjugate.

The structural integrity of the multicomponent system has been confirmed performing spectral, computational and electrochemical studies.



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Multifunctional nanogels from e-beam irradiation of PVP aqueous solutions, only

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Nanogels (NGs) are 3D networks of crosslinked hydrophilic polymers with nanoscale dimensions. Due to their structure and physico-chemical properties, they are a promising nanomaterial platform for site-specific drug delivery and diagnostic nanodevices. Considering the intended application, biocompatibility is a requirement, but also a simple and easy to scale up synthetic process is highly desirable. In this perspective, high energy radiation processing is a valuable option. In fact, simply starting from dilute or semi-dilute aqueous polymer solutions, it is possible to synthesize multifunctional NGs with tunable properties, with no employment of organic solvents, initiators or catalysts. Due to the high amount of imparted energy, hydroxyl radical (OH^\cdot) is formed as water radiolysis product, which has a key role on the NGs formation and functionalisation. In fact, OH^\cdot is the mainly responsible of the introduction of radical sites on the polymeric chains, which may differently arrange themselves, depending on the system composition and irradiation conditions.[1] The formation of the 3D network is essentially related to inter/intra molecular crosslinking reactions, while radical-radical disproportionation or macroradicals reaction with molecular products formed upon water radiolysis, are involved in the introduction of several functionalities (*i.e.* - NH_2 , - COOH), useful for the decoration of NGs with the desired ligands, therapeutic molecules, fluorescent probes, etc. In this work, we will show that irradiation forms on an chemically inert water-soluble polymer, poly(N-vinyl pyrrolidone), functional groups that can be used to covalently conjugate insulin in the prospect of developing a nanosystem to deliver insulin to the brain for the treatment of neurological disorders, such as Alzheimer Disease. [2]

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Selective transfer hydrogenolysis of benzyl phenyl ether promoted by Pd/Fe₃O₄ catalyst

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The selective cleavage of C-O single bond preserving the aromatic nature represents one of the major challenges in the catalytic valorization of lignin [1].

In the last years, the co-precipitate Pd/Fe₃O₄ catalyst shown a powerful and efficient performance in the catalytic transfer hydrogenolysis (CTH) of lignocellulosic platform derived molecules. [2-4]

In this context, the selective cleavage of the C-O bond of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE) - as model compounds of lignin linkages - was investigated, under CTH conditions using 2-propanol as the H-donor and the Pd/Fe₃O₄ catalyst with a nominal palladium loading of 5 wt %.

The use of this catalyst, shown an appreciable BPE (0.1 M) conversion (19.7%) that increases by increasing the reaction temperature and, at 240 °C, it is fully converted (100% conversion) into phenol and toluene as the only reaction products (100% aromatic yield) clearly indicating that the cleavage of the etheric C-O bond occurs as the primary reaction route under CTH conditions.

In the next step, the H-donor ability of simple primary (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and secondary (2-butanol, 2-pentanol and 3-pentanol) alcohols was tested and a tight relationship between the moles per l of aldehyde or ketone formed (H-donor ability) and the amount of BPE converted (moles per l) was observed.

Reaction of PPE at 240 °C shows a lower conversion (22%) and 100% yield of aromatics. On the contrary, DPE was not converted at all. Interestingly, a linear correlation of the bond strength and the ability of the Pd/Fe₃O₄ catalyst in the CTH of aromatic ethers was found.

Therefore, the Pd/Fe₃O₄ catalyst is able to cleave the C-O bond of benzyl phenyl ether (BPE) and 2-phenethyl phenyl ether (PPE) under CTH conditions and, at the same time, avoid parallel hydrogenation reactions of the aromatic ring, being one of the most selective heterogeneous catalysts in the production of arene derivatives.

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Vicinal effect in the Ring Opening Polymerization (ROP) of lactones

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For this work, at first we have studied the acid catalysed lactonization of several γ -hydroxyesters, bearing methyl substituents at different positions.

A ^1H -NMR kinetic study of this set of monomethyl and/or gem-dimethyl substituted esters in CDCl_3 was carried out. We evaluated the effect of the leaving group (ethyl vs. i-propyl ester) and the catalyst efficiency. We found that i) a monomethyl substitution produces a lowering of the energy barrier similar to that of a gem-dimethyl substitution (Thorpe-Ingold effect), ii) the ring closure of i-propyl esters is slower than that of ethyl esters, iii) strong acids are more efficient than weak acids according to the Brønsted relationship, and iv) the Thorpe-Ingold effect is not just an intrinsic feature of the linear precursor but it depends on the catalyst as well.^[1,2] Quite surprisingly not so many reports about the effect produced by the presence of two substituents in a vicinal relationship are present in literature.

So, prompted by this strange "black hole" in literature, we would like to give an explanation and clarify three issues: i) how is the cyclization affected by the vicinal substitution? ii) is the effect stereospecific, that is to say, dependent on the diastereomeric relation (*syn* or *anti*) between the two vicinal substituents? iii) is it possible to observe a stereospecific effect in the Ring Opening Polymerization (ROP) of lactones as well?

Preliminaries studies on model compounds indicate that the *vic*-disubstituent effect is not only stereospecific, since the *anti* linear precursors undergo to the cyclisation reaction much faster than the corresponding *syn* diastereoisomers, but it is more efficient than the above mentioned Thorpe-Ingold effect.

Indeed, the *anti* vicinal substituted adduct is faster than the *gem*-disubstituted of about 4 times in the lactonization reaction.

Interesting results are obtained in the ROP process too, in which *vic*-disubstituted δ -lactones show a stereospecific polymerization (in a ratio of around 1 to 5), dependently of the diastereomeric configuration of the monomer.

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Bio-ethanol production from crystalline cellulose promoted by the heterogeneous PdFe catalyst

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Lignocellulosic biomass is the most promising source, being the most abundant, inexpensive, renewable, inedible and CO₂-neutral raw material available on the earth. Currently, the direct cellulose conversion into valuable chemicals is one of the main challenges in green chemistry, since, at present, its transformation consists of multiple steps including hydrolysis to glucose, followed by its hydrogenation to polyols [1].

Recently, the co-precipitated Pd/Fe catalyst gained considerable attention [2-3] and has been deeply investigated in several catalytic reactions including hydrogenolysis, catalytic transfer hydrogenolysis (CTH) of polyols and aromatic/aliphatic esters, and aqueous-phase reforming (APR) of polyols [3-5].

The one-pot conversion of crystalline cellulose into valuable products, in water, in mild operating conditions promoted by the Pd/Fe catalyst is the aim of the present work. The process is feasible under H-transfer conditions, without the direct addition of a reducing agent, because the hydrogen necessary for the hydrogenolysis reactions is supplied from the APR and the water-gas-shift (WGS) processes.

These findings could have significant implications for the sustainable bio-ethanol production practicable under heterogeneous catalyst, in only one step, by using lignocellulosic biomasses as starting raw material.

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Synthesis of Novel Bispidine Ligands and their Coordination Polymers

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Metal organic frameworks (MOFs) are coordination polymers (CPs) based on the combination of organic ligands and metal ions, which assemble in the solid state into porous materials.¹ Over the last years, MOFs have gained increasing attention for their potential in a range of applications, such as chemical purification, molecular sensing, gas storage and catalysis.² Among the most common classes of MOF ligands, carboxylic acid and pyridine based compounds are predominant.

Bispidine compounds, derivatives based on the 3,7-diazabicyclononane scaffold, are well known in the literature and they can be conveniently prepared through a multicomponent approach, by a cascade sequence of Mannich reactions of an activated ketone with an amine and an aldehyde. Moreover, even though they have been reported as efficient metal ions binders, they have never been employed as ligands for the construction of MOF systems.

Here, we present the synthesis of a series of new 9-oxo-bispidine ligands decorated with two pyridine rings having their *N* donor atoms arranged in a divergent way, thus allowing for coordinative polymerization with metal ions. These ligands have been employed to obtain CPs as single crystals and microcrystalline powders, which have been characterized in detail by X-ray crystallography. This work represents the first study on CPs based on the bispidine unit and the data obtained are quite promising for the development of novel responsive coordination polymeric materials; in particular, it has been demonstrated by XPRD analysis that one of the microcrystalline materials obtained can undergo two consecutive solvent guest exchange transformations.

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Smart Materials for Active Packaging

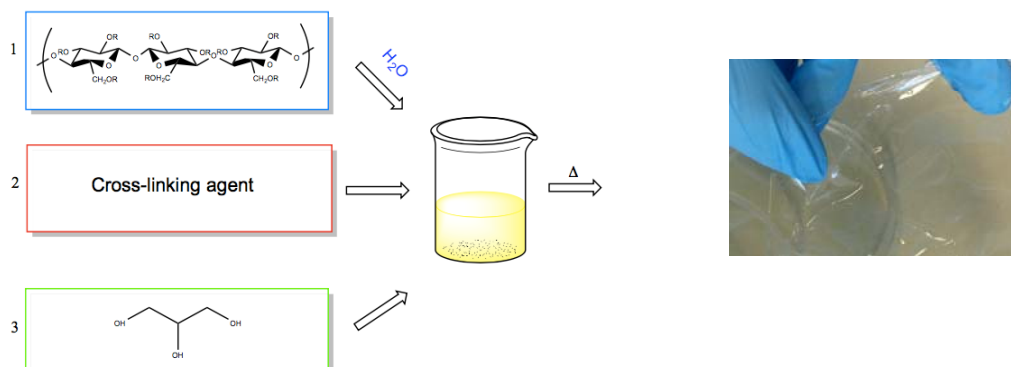
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In response to the increasing environmental concerns, there is an extensive research effort on using renewable resources to create sustainable and biodegradable food packaging systems, in order to substitute petrochemical derived plastics. An environmentally friendly and attractive feedstock for bioplastics is carboxymethylcellulose (CMC), a cellulose ether that can potentially form excellent films due to its polymeric structure and high molecular weight chains. CMC can be cross-linked, thanks to the presence of carboxyl and hydroxyl moieties, in order to reinforce the intramolecular binding by introducing covalent bonds. In our recent work, we have demonstrated the possibility to carry out this reaction in the presence of a selective condensation agent which leads to the cross-linked product. Glycerol has been used as plasticizer, to provide a more flexible structure. Films were prepared in a very sustainable and simple way, under mild reaction conditions. Antimicrobial activity may be imparted to the film by addition of an antimicrobial agent. In a flask provided with magnetic stirring, an equivalent of CMC was dissolved in water. To the solution were then added up to 50% w/w of glycerol and 5-10% w/w of cross-linking agent. The solution was stirred for 4 hours, then placed in a vessel and oven dried for 18 hours at 70 °C. Mechanical and physical properties of the films obtained reveal a good elasticity and transparency. Characterization of the films has been carried out also by FT-ATR spectroscopy, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM). In conclusion, a simple and economically convenient protocol has been devised allowing to obtain sustainable bio-derived antimicrobial films suitable for food packaging.



Scheme 1. Procedure for the preparation of antimicrobial CMC film

Development and prospects of nanostructured smart systems for crop protection

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In recent years, climate change and globalization of the market have stimulated the diffusion in our country of different plant pathogens, causing serious economic damage to agriculture. In particular, the southern Apulia region is recently the protagonist of this scenario due to the spread of The Olive Quick Decline Syndrome, denoted CoDiRO, that is associated to *Xylella Fastidiosa* infection [1]. Currently there is no cure for infected trees. Therefore, the research of control strategies is still a current topic. The success of nanomedicine has paved the way for the development of agri-nanotechnology. For that reason, the as-synthesized CaCO₃ nano-crystals (nanoCaCO₃) were tested as innovative antibacterial nanomaterial against the pathogen *Xylella fastidiosa*. NanoCaCO₃ interaction with bacteria was studied through cells ultrastructural analysis by transmission microscopy. CaCO₃ nanocrystals affect *X. fastidiosa* causing bacteria wall alteration up to cell destruction [2]. The action of this nanomaterial will be thorough with *in planta* experiments. We are analyzing the absorption of nanocrystals into rooted olive cuttings. A good alternative to inorganic systems is represented by Nanocellulose [3]. We are investigating the preparation of nanostructured materials using Nanofibrillated cellulose by TEMPO-mediated oxidation of cellulose [4]. The aim is the encapsulation of different agrochemicals for crop protection.

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Synthesis, aggregation properties, and computational investigation on a series of bis(salicylaldiminato)zinc(II) Schiff-base complexes varying the bridging diimine

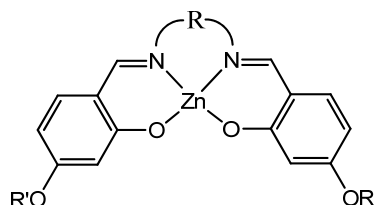
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Bis(salicylaldiminato)zinc(II) Schiff-base complexes, ZnL, are characterized by interesting photophysical and aggregation properties.¹⁻⁴ Most of these properties can be related to the Lewis acidic character of the Zn(II) metal centre. In fact, in absence of Lewis bases these complexes are stabilized through intermolecular Zn...O axial interactions with formation of dimeric or supramolecular aggregates, while in the presence of Lewis bases are stabilized as monomeric, ZnL-base, adducts. Here we report a detailed combined computational/experimental analysis on a series of ZnL complexes changing the structure of the 1,2-diimine bridge, R, in order to investigate the sterical and electronic features responsible for their Lewis acidic character.



Calculated binding constants for the formation ZnL-pyridine adducts are in excellent agreement with experimentally derived values. This allowed establishing a relative Lewis acidity scale within the involved series. While the complex derived from the non-conjugated ethylenediamine possesses the lowest Lewis acidity, the complex derived from the diaminomaleonitrile is the stronger Lewis acidic species. The different Lewis acidic character along the series is governed by the relative stability of the ZnL-pyridine adducts with respect to the dimers. These are relevant features for the sensing and catalytic properties of these complexes.

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Poly-acrolein microspheres functionalized with cobalt corroles for chemical sensor applications

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The recent synthetic protocols developed for the corrole synthesis and functionalization [1,2] lead to application of this macrocycle in different fields, such as catalysis, photochemistry and medicine [3]. Some recent works have already pointed out the possible application of this macrocycle in the chemical sensor field: cobalt corroles are able to coordinate selectively carbon monoxide [4], and many corroles demonstrate better performances as sensing material compared to porphyrin analogs [5]. In this work, we have been interested in the investigation of composite materials, where corroles have been integrated with polymeric structures. The functionalization of the cobalt corrole scaffold with an acrolein substituent, enabled its copolymerization with pure acrolein, leading to functionalized poly-acrolein monodispersed microspheres (average diameter = 700 nm). The sensing properties of layers of particles were investigated with nanogravimetric transducers. The hybrid material revealed a large enhancement in responses and sensitivity for all the tested analytes, compared to the individual constituents. This new material not only optimizes the ability of the corrole as sensing material, but also takes advantage of the properties of the polymer itself, leading to a material with unexpected capability.

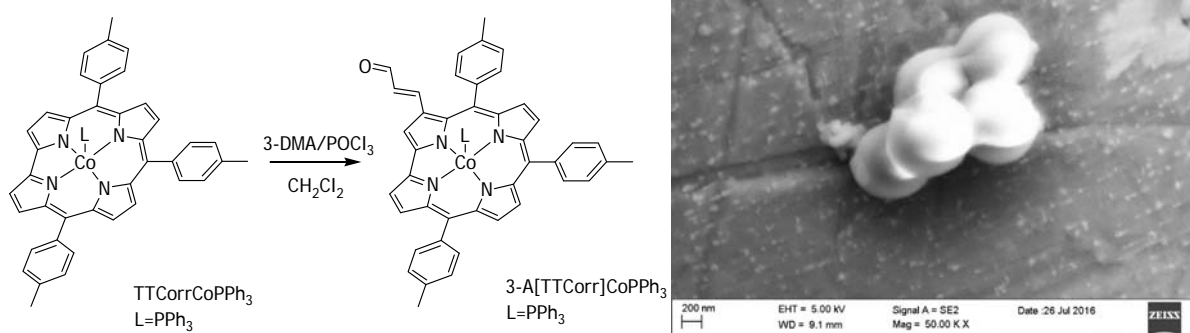


Figure 1. Functionalization of cobalt corrole (left) and SEM image of corrole functionalized poly-acrolein microballs (right)

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Light-triggered release of natural active agents from polymeric nanocapsules

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Light-responsive polymer capsules can provide an excellent tool for the targeted and controlled delivery of drugs and active agents [1]. This work reports on the preparation and characterization of light-responsive nanosized capsules loaded with a natural active agent and coumarin-6 as a model drug. Nanocapsules based on a polyamide containing azobenzene moieties in the main chain were prepared via interfacial polycondensation in o/w miniemulsion [2]. Noticeably, azobenzene undergoes E-Z photo-isomerization when irradiated with UV-light ($\lambda=365\text{nm}$), resulting in massive rearrangements in the polyamide shell and release of the core material. Shape and morphology of the nanocapsules were observed via electron microscopy (SEM and TEM). The kinetics of release of the encapsulated active agent and coumarin 6 was assessed by UV-Vis spectroscopy and spectrofluorimetry, respectively. The results validated the efficiency and reliability of the release mechanism confirming their suitability for a wide range of applications, such as drug delivery, cosmetics and household products.

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Polycarbonate/Carbon Nanotube/TiO₂ Composite Photoactuators for Chemical Applications

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Photoactuators, namely systems able to convert light into mechanical work, are among the most studied actuators, offering exciting options for energy harvesting, smart sensing and soft robotics.^[1] Over the years, a variety of systems has been studied, ranging from gels or liquid crystals containing photoactive molecules, to bimorph systems.^[2] One strategy that has been extensively investigated is the combination of materials characterized by different coefficient of thermal expansion (CTE), such as polycarbonate (CTE=65-70 ppm/K) and Single Wall Carbon Nanotubes (CTE=3-4 ppm/K). During illumination, SWNTs absorb light and convert it into heating. As a consequence of the CTE mismatch, during illumination the polycarbonate layer is more expanded than the SWNT layer, resulting in a macroscopic curling of the whole structure in the direction of the SWNT side.^[3] These systems have been already applied for the preparation of macroscopic demos of smart curtains, oscillating wheels and soft robots. In this work, we will show how this type of photoactuators can offer many opportunities also for chemistry. In particular, we propose a new type of smart catalyst, which can be used for the photomechanical activation or inhibition of chemical or photochemical reaction (i.e. local explosions, polymerizations or photodegradations) with precise spatial control. This goal has been pursued by combining the polycarbonate/SWNT bimorph actuators, with TiO₂ nanoparticles. In fact, the addition of TiO₂ NPs to SWNT slurry, on one hand enhances the reproducibility and the homogeneity of the photoactuation of the bimorph photoactuators, making phototropic actuation constant, fast, and perfectly reversible; on the other, it provides a photocatalytic activity to the whole system, which can be further exploited. Our results suggest that the integration of photocatalysts with soft photoactuators can open intriguing opportunities for both chemistry and soft robotics.

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Domino reaction for the controlled functionalization of sp^2 carbon allotropes

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Graphene and graphene related materials are a hot research topic in the material science and are becoming a reality of increasing importance in many application fields. Indeed, graphene has high charge-carrier mobilities, in-plane thermal conductivity and very high elastic modulus. It is increasingly acknowledged that application of carbon nanomaterials such as graphene has to be assisted by functionalization, which allows to tune electronic and solubility properties, phase-forming and self-assembly behaviour.

In this work, functionalization of graphene layers was performed with 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP) [3].

SP is a serinol derivative obtained from the neat reaction of 2-amino-1,3-propanediol with 2,5-hexanedione, with atom economy of about 85%, almost quantitative yield and thus high atom efficiency, the only byproduct being water, in the absence of solvent and catalyst [1, 2, 3]. Functionalization was obtained by simply mixing nanosized high surface area graphite with SP, giving either mechanical or thermal energy. Very high functionalization yield was found, larger than 90% and even almost quantitative. Few layers graphene were isolated from stable water suspensions. Reaction of SP was applied to other sp^2 carbon allotropes, such as carbon nanotubes and carbon black. Many different applications were developed: from conductive inks to carbon papers and aerogels.

The reaction occurring between SP and graphene layers was investigated. Adducts of a high surface area nanosized graphite were prepared with a model molecule, 1,2,5-trimethyl-1*H*-pyrrole (TMP). Pristine TMP, HSAG, products formed by the reaction and HSAG-TMP adducts were studied by means of Fourier transformed infrared spectroscopy (FT-IR), ^1H -NMR and thermogravimetric analysis. DFT modelling was carried out to predict IR spectra of HSAG-TMP reaction products and adducts. Reaction pathway is presented. Domino reaction appears to occur: carbocatalyzed oxidation of the pyrrole compound lead to the formation of activated double bond, able to give rise cycloaddition with the graphitic substrate. Such a facile and sustainable functionalization method allows the controlled introduction of functional groups on graphitic substrate without appreciably altering their structure.

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Synthetic strategies for tailoring the performances of Carbon/Mg(OH)₂ materials for thermochemical heat storage application

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MgO/H₂O/Mg(OH)₂ thermochemical system stores heat (200-400°C) through the dehydration of Mg(OH)₂ and releases the stored heat when required by the reversible hydration of MgO in presence of water vapour. Nowadays, this system is at an early stage of development [1]. To bring this technology at an applicative stage, several research efforts are performed on the material development. In this study, it has been investigated for the synthesis of exfoliated

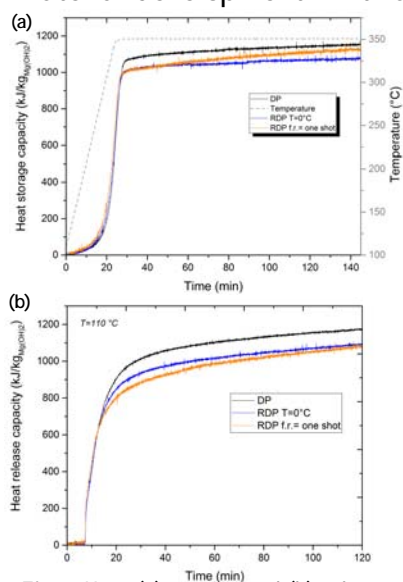


Fig. 1 Heat (a) storage and (b) release capacities.

graphite (EG)-Mg(OH)₂ hybrid materials the influence of two preparation methods: Deposition-Precipitation (DP) and Reverse Deposition-Precipitation (RDP). The effect of these two approaches on the EG/Mg(OH)₂ morphology and crystal structure and their impact on Mg(OH)₂ thermochemical behavior have been evaluated. Regarding to the RDP method, it has been examined how the reaction parameters (i.e. temperature, precipitating-agent feeding rate) affect EG/Mg(OH)₂ morphological and structural aspects and how these are related to the thermochemical performances of the heat storage material. The highest heat storage/release capacity can be achieved by EG/Mg(OH)₂ obtained by Deposition-Precipitation and Reverse Deposition-Precipitation

realized through one shot addition of the precipitating agent and at 0°C. As inferred in Fig. 1, a heat storage/release capacity of 1166, 1163 and 1080 kJ/kg_{Mg(OH)₂}, respectively, has been obtained approaching the maximum theoretical value of ~1300 kJ/kg_{Mg(OH)₂}.

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Poly(phenylene sulfide sulfone), polymer electrolyte with improved oxidation stability for redox flow battery applications

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Redox flow batteries (RFBs) are one of the most promising technologies in terms of large-scale energy storage.¹ Among other possibilities, vanadium RFBs (VRFBs) is the most mature technology. The two half-cells are separated by an ion exchange membrane, whose primary function is to allow the proton flow, while preventing the transport of vanadium species. Although Nafion membranes are commonly used for RFBs thanks to the high ion conductivity and chemical stability, the low selectivity causes a significant drop of the battery performances over time. To overcome this issue, hydrocarbon-based membranes, such as sulfonated poly(ether ether ketone) (sPEEK), have been also extensively tested because highly rigid aromatic macromolecular chains and tinier ionic clusters are expected to decrease the active species crossover. However, sPEEK membranes suffer from poor chemical stability in VRFB medium.² In this study we propose sulfonated poly(phenylene sulfide sulfone) polymers (sPSS) as a more chemically stable alternative to sPEEK.

Battery tests highlighted comparable performances and lower capacity losses due to lower vanadium crossover through the sPSS membrane with respect to Nafion and sPEEK, this was explained by narrower network of the hydrophilic channels inside the polymeric matrix, as was studied by thermoporosimetric analysis. Moreover, while sPEEK membranes considerably degraded in VO_2^+ solution and lost their integrity in the time scale explored, sPSS underwent oxidation of the sulfide to sulfone bonds, thus preventing the macromolecular chain breakdown.

Acknowledgements

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Engineering Crystalline Supramolecular Rotors via Halogen Bonding

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Amphidynamic crystals are materials built to possess rapidly moving components in the solid state. Nowadays there is a growing interest in this class of compounds for the development of new functional materials and molecular machines. [1]

The aim of our research is to take advantage of crystal engineering principles to assemble stators and rotators into cocrystals showing highly efficient molecular dynamics. This strategy has few advantages such as its intrinsic flexibility and hence the trivial access to a vast number of different supramolecular rotors. Firstly, we were able to synthesize crystalline supramolecular rotors selfassembled by halogen bonding (XB) of diazabicyclo[2.2.2]octane (DABCO), a well known D_{3h} -symmetric cylindrically shaped rotator, and a set of five fluorine-substituted iodobenzenes, acting as strong halogen bond donors, that take the role of the stators. The obtained amphidynamic cocrystals show excellent dynamics performance and XB works both as self-assembly driving force and main axle of rotation. [2]

Based on these results, we designed and synthesized a series of isomorphous amphidynamic cocrystals based on XB. By carefully studying their inner dynamics and thanks to their structural similarities, we were able to distinguish the enthalpic and entropic components of the rotational free energy barrier. What is more, one of the cocrystal show the lowest ever-reported activation energy of the rotational process. [3]

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Structural and Thermodynamic Properties of Transition Metal Ions in Room Temperature Ionic Liquids (RTILs)

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Room temperature ionic liquids (RTILs) have attracted much attention as a “green” alternative to classical organic solvents owing to their negligible vapor pressure, non-flammability, thermal stability, wide electrochemical windows, solvation ability and (supposed) low toxicity. The strong correlation between structure and physico-chemical properties allows to select a RTIL with optimal features for a specific task. Due to these characteristics, RTILs are interesting solvents for a variety of applications such as separations, extractions, catalysis, electroplating, batteries and solar cells.¹

Despite many of these applications involve transition metal ions and complexes, few structural and thermodynamic data on metal solvation are available.² A better definition of their solvation structure and thermodynamics in RTILs is therefore of fundamental importance to improve our understanding of metal ions behavior in these media. In this work, theoretical methods (molecular dynamics simulations, DFT calculations) have been applied to obtain a picture at molecular level of the metal ions solvation in widely used imidazolium-based RTILs. In particular, we focused on Zn^{2+} and Ag^+ ions, since the solvation free energies in $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ can be estimated from experimental data.³ Different sets of Lennard-Jones parameters for the metal ions have been tested to reproduce Gibbs free energy of solvation/transfer from water. Metal coordination number, bond distances and binding mode of the IL (Figure 1) have been analyzed and compared with available data.

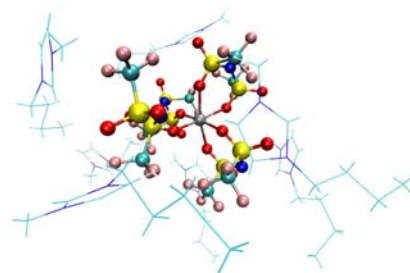


Figure 1: snapshot from MD trajectory of $\text{Zn}(\text{II})$ in $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ (1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). Balls and sticks: $[\text{TF}_2\text{N}]^-$ anions; lines: $[\text{C}_4\text{mim}]^+$ cations.

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Cellulose based materials: from environmental application to controlled drug release

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Thanks to its high availability, low cost and good biocompatibility cellulose is widely employed as starting material for preparing a high numbers of materials with different applications. In particular cellulose nanofibers (CNF) are proven to be versatile in many preparations. The regioselective oxidation of the C6 primary hydroxyls of the anhydroglucose units of cellulose catalyzed by TEMPO in presence of NaBr/NaClO system allows to prepare CNF nano-dimensioned (TOCNF).^{1,2}

Recently our group synthesized a new class of all-organic cellular solids combining TOCNF and branched polyethyleneimine (bPEI). The resulting sponge-like materials show high performances in removing contaminants from water (e.g. heavy metal ions and phenolic compounds).³ The same synthetic protocol has been also extended to generate a novel material functionalized with pNO₂-phenyl-urea units for the heterogeneous and selective sensing of fluoride anions in DMSO solution.⁴

Furthermore, we have investigated the role played by the addition of citric acid (CA) as co-crosslinker. The new materials were characterized from a chemical (FT-IR, 13C and 15N CP-MAS NMR spectroscopies), structural and mechanical point of view. The materials possess the interesting capability to recover their shape with reduced losses in mechanical resistance, while their Young's Modulus progressively increased with the content of CA. Moreover, quantitative information on the porosity of the materials and their inner microstructure has been obtained by Micro-Computed Tomography (μ -CT) analysis.

In order to investigate the possible application of bPEI-TOCNF sponges for the release of active principles, they have been used it for adsorption and release of two model drugs, amoxicillin (AM) and ibuprofen (IB). All materials showed very good performances in adsorbing both AM and IB (~200 mg g⁻¹) from methanol solution. Interestingly, samples reticulated in presence of CA showed slower kinetic release in aqueous environments than materials obtained without CA.⁵

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Lithium polysulfide catholyte for lithium-sulfur batteries

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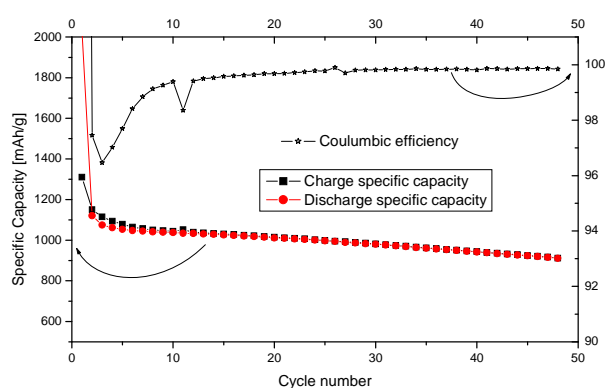
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Sulfur is a promising cathode material, with a theoretical lithium capacity of 1675 mAh/g for complete reduction to Li_2S [1]. However the insulating nature of sulfur deposited in the electrode cause low utilization of active material and poor cycle life[2]. To enhance the performance of active material one of the most promising strategy provides to transform the sulfur in lithium polysulphides[3].

A electrochemical behavior of a solution of Li_2S_8 polysulfides used as active material in a lithium/sulfur semi-flow battery was studied. The synthesis of polysulfides was performed in a mixture of dioxolane/dimethoxyethane 1:1 DOL/DME.

Electrochemical characterizations were performed with 2032-type coin cell, using lithium metal as the anode and the reference electrode. The tested batteries shows high specific capacity about 1 Ah/g. Furthermore these cells present high stability: during 50 cycles the fading of capacity is about 0.4%. The coulombic efficiency is close to unit: this result indicates the high reversibility of the reduction of Li_2S_8 to Li_2S and the following oxidation to S.

The electrochemical tests confirm that lithium polysulfide are very promising active materials for hybrid Li/S battery.



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Molecular Tailoring of Phenothiazine-Based Hole-Transporting Materials for High-Performing Perovskite Solar Cells

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Since the pioneering report by Miyasaka *et al.* in 2009,¹ organic-inorganic lead halide perovskites have rapidly become the hottest topic in photovoltaics due to their excellent light-harvesting from visible to near-infrared wavelengths with high extinction coefficients and long electron-hole diffusion lengths.² The free photo-generated holes within the perovskite material need to be extracted and transported by hole-transporting materials (HTMs). To date, the highest reported efficiency values have been reached with the expensive Spiro-OMeTAD.³ Novel phenothiazine-based HTMs, PTZ1 and PTZ2, have been synthesized through straightforward Buchwald-Hartwig and Suzuki-Miyaura cross-couplings, respectively, by binding the suitable donor groups (diarylamine or triarylamine) to a phenothiazine core and proven for the first time in perovskite solar cells. A dramatic effect exerted by the presence of phenylene spacers was observed on the relevant photovoltaic performances. The power conversion efficiencies measured under AM 1.5 sun shoot up from 2.1% (PTZ1) to a remarkable 17.6% (PTZ2), a value rivaling those obtained with the state-of-the-art Spiro-OMeTAD (17.7%). The dramatic difference in photovoltaic performances exhibited by the two phenothiazine-based derivatives can be attributed to the modulation of electron density distribution, which controls the stability of molecules during the charge transfer dynamics at the perovskite/HTM interface. These results indicate phenothiazine-based materials as promising candidates to be used as readily available and cost-effective alternatives in perovskite solar cells.

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Iron doping and Ba deficiency in $\text{NdBaCo}_2\text{O}_{5+\delta}$ Cathodes for IT-SOFCs

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Co-based double perovskites ($\text{LnBaCo}_2\text{O}_{5+\delta}$ Ln=Lanthanides or Y) have been recently proposed as cathode materials for IT-SOFCs (1, 2). These compounds crystallize in a double perovskite structure ($\text{LnCoO}_{3-\delta}\text{-BaCoO}_{3-\delta}$), where Ln and Ba ions sit on alternated single perovskite layers. Pr, Nd and Gd based compounds show the best performance, likely due to their optimum ion size. The effect of Fe-doping on the B-site and of Ba deficiency on the A-site have been investigated: XRD, TG-DTA, ICP-MS and cerimetric titrations were performed to assess the phase composition, crystal structure, chemical composition and oxygen content. The electrochemical properties were investigated via 4-probe electrical conductivity measurements and Electrochemical Impedance Spectroscopy on symmetrical cells with GDC electrolyte. All the compounds show high total electrical conductivity (between 400 and 600 S/cm at 700 °C). A tenfold decrease of the area specific resistance is observed at increasing Ba deficiency to 10%. Detailed equivalent circuit analysis reveals that the effect of Ba is associated with a promotion of the bulk diffusion steps at high frequency. Iron substitution triggers a structural change from orthorhombic to tetragonal, and lowers the electrical conductivity. The compound with 20% of iron shows the lowest polarization resistance (0.17 $\Omega\cdot\text{cm}^2$ at 700°C). The ORR mechanism investigated by ECM and physical 1D modeling shows that the first electronation of the oxygen atom on the MIEC surface and the bulk diffusion of the oxygen vacancies in the MIEC lattice are the rate determining steps.

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Study of two different Artificial Pinning strategies in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films deposited by Metal Organic Decomposition method

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$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) film grown by metal organic decomposition (MOD) is a promising candidate for high performance HTS cables¹⁾. Moreover, artificial pinning centres (APC) inclusions improve the current transport performance of the films both in high magnetic fields and temperatures.

In this work we investigate two different pinning strategies: BaZrO_3 (BZO) nanoinclusions grown via MOD together with the superconducting film, and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) nanoislands grown in a preliminary step via polymer assisted deposition (PAD)²⁾ and then used as substrate for the deposition of YBCO via MOD³⁾. We thoroughly analyze the properties of YBCO thin films with different BZO mol. percentage deposited on SrTiO_3 single crystals obtained from a low fluorine 0.2M coating solution. Morphology and crystalline structure of superconductor films were deeply investigated by using scanning electron transmission, and atomic force microscopies, X-ray and X-ray photoelectron spectroscopy. Superconducting properties, assessed through electrical and magnetic analyses, were evaluated at different temperatures (from 10 K to 85 K), magnetic field directions and intensities (0-12 T). LSMO solutions were prepared with different concentration and deposited on different substrates (SrTiO_3 , Y_2O_3 stabilized ZrO_2 , MgO) via PAD. The as obtained samples were characterized via AFM and XRD. Selected samples then acted as substrate for the growth of the superconducting film of YBCO via MOD. Preliminary results revealed good YBCO structural and superconductive properties defining this method as promising for the realization of YBCO films with improved vortex pinning properties.

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Ceramic templated melanin nanostructures: a novel synthesis approach to bio-functional hybrid materials

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Organo-inorganic hybrids provide the opportunity to invent a huge set of new multifunctional materials with a large spectrum of known and as yet unknown properties. Melanins, hydrophobic natural pigments are emerging as a powerful organic component for developing biologically active materials because of their numerous biological functions, such as photo-protection, photosensitization, free radical quenching, metal ion chelation and even intrinsic antimicrobial behavior. Furthermore, due to their semiconductor behavior and electrical properties they hold great promise for next-generation photovoltaics and bioelectronics. Melanins are produced in-vivo by the oxidative polymerization of phenolic or indolic compounds within melanosomes that are believed to template melanin formation. Following a bioinspired approach, herein we propose a novel synthesis strategy towards hybrid materials, that exploits inorganic ceramic systems as catalysts and structure directing agents in melanin biopolymers building up. In this route we disclosed TiO₂ ability to drive 5,6-dihydroxyindole-2-carboxylic acid (DHICA) polymerization via complex mediated electron transfer (LMCTC) from DHICA to the TiO₂ lattice, that enables photo-activation under visible light [1]. This strategy led to eco-friendly melanin-TiO₂ hybrid nanostructures with unique antimicrobial activity even under visible light (Fig.1) [2,3]. This approach was successfully extended to other semiconductor oxides, such as LaFeO₃ perovskite, thus providing the key to optimize interactions between the organic and inorganic components and overcome limiting transport mechanisms. Finally, this synthesis strategy was carried out to the design of novel eumelanin-silica hybrid nanoparticles, integrating the potent antioxidant properties of DHICA melanin into a stable, bioactive and biocompatible silica scaffold (Fig.2). These systems prove that melanin's biofunctional and physical-chemical properties can be markedly enhanced, if its formation occurs through templated polymerization in the presence of a ceramic phase, disclosing the manifold potentialities of this approach, that can ultimately lead to cutting-edge functional hybrid materials featuring relevant biological properties, such as antimicrobial activity, selective cell interaction and signaling, as well as ionic- and electronic-based charge transport behavior.

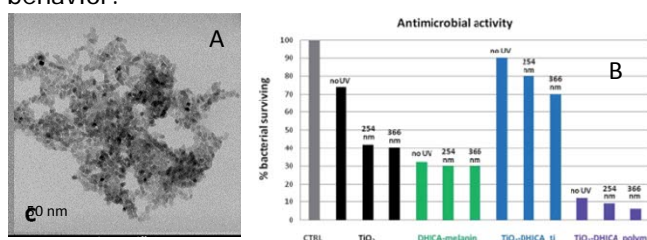


Fig. 1 TEM micrographs (A) Antimicrobial activity (B) of TiO₂_Mel nanostructures

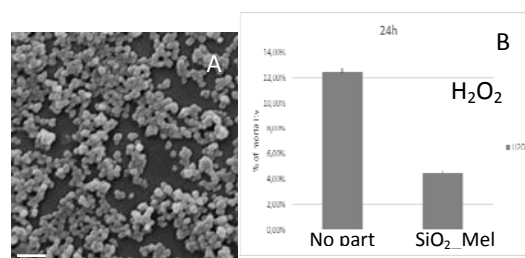


Fig. 2 SEM micrograph (A) and antioxidant properties (B) of SiO₂_Mel nanostructures

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Chemical characterization of organic-inorganic hybrids synthesized via sol gel for the biomedical field

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Organic-Inorganic hybrids (OIHs) are materials consisting of organic and inorganic components interpenetrated on scales of less than 1 μm . The leading idea in their development is to retain the best properties of each component and to overcome their drawbacks. The nature of the bonds between the two phases has an impact on the properties of the materials. Therefore, Judenstein P. et. al [1] proposed a classification of the OIHs based on the interactions between the phases. They indicated those materials as first or second class OIHs, depending on whether weak bonds (hydrogen bond, Van der Waals forces, etc.) or strong bonds (covalent or ionic-covalent bonds) between the constituents respectively occur. An ideal technique to synthesize OIHs is the sol-gel method. It is a versatile process used to prepare glass and ceramic at low temperature. The transition of the system from a mostly colloidal liquid ('sol') into a solid 'gel' involves the hydrolysis of metal alkoxide precursors in a water-alcohol solution and condensation reactions. The low processing temperature allows of entrapping thermolabile molecules (e.g. polymers and drugs) in the inorganic matrix, producing OIHs. In the present work, different percentages of polyethylene glycol (PEG) were embedded in an inorganic ZrO_2 matrix. The obtained materials were extensively characterized by several instrumental techniques (SEM, XRD, FTIR and solid-state NMR) which proved that amorphous and homogeneous first class OIHs were obtained [2]. Moreover, in vitro tests proved that these materials were bioactive and biocompatible and, thus, potentially suitable for biomedical applications. Therefore, afterward the materials were successfully used to prepare coatings, capable of improving biological response of bioinert implants, and matrices for drug delivery, in which PEG amount modulated the release kinetic of the drug [3].

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Photocured siloxane polymers for genomic microfluidic applications

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Microfluidic devices represent an emerging technology with a great potential in analytical life sciences [1]. In particular lab-on-a-chip concerning genomic applications have attracted great interest; in such systems there is often the need to provide an efficient DNA amplification by PCR (Polymerase Chain Reaction) [2].

Nowadays polymers are the materials of choice for the fabrication of microdevices for genomic applications. In the present work, we introduce the use of a class of photocured siloxane polymers for the fabrication of microfluidic devices for biomedical applications (i.e., PCR). New multifunctional acrylic oligomers are synthesized [3] and then photocrosslinked. Moreover, copolymerization is used as strategy to optimize the photopolymer properties. The polymers and copolymers synthesized are suitable for biomicrofluidics: they are PCR compatible, highly resistant to temperature and various solvents, transparent, dimensionally stable and essentially non-permeable to water vapor. Therefore, these materials are used to fabricate microfluidic devices, in which PCR is successfully conducted as proof of principle.

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Master curves for the mechanical reinforcement of diene elastomers with sp^2 carbon allotropes

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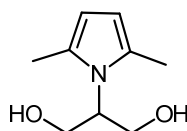
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sp^2 carbon allotropes are efficient reinforcing fillers for polymer melt and elastomers: carbon black (CB) has been used since early 1900's and nanofillers such as carbon nanotubes (CNT), graphene and graphene related materials (GRM) have increased their importance over the last decades. Nanofillers can definitely establish larger interfacial area with the polymer matrix than CB and great impact on material properties is thus expected. However, it is widely acknowledged that they will not be able to completely replace CB. Hence, increasing research efforts are on hybrid systems based on CB-CNT and CB-GRM [1]. Research objective is to identify common features and behaviour of nano (CNT, GRM) and nanostructured (CB) sp^2 carbon allotropes.

In this work, initial modulus was determined by means of dynamic-mechanical shear measurements of composites based on either poly(1,4-cis-isoprene) or poly(styrene-co-butadiene) as the rubber and either CB or CNT or GRM or hybrid systems as the reinforcing fillers.

Filler-polymer interfacial area (i.a.), calculated as the product of filler surface area, density and volume fraction, was used to establish a common correlation with the composite initial modulus. A sort of master curve was derived, able to fit all the points up to interfacial area of about $27 \mu\text{m}^{-1}$, corresponding to remarkable filler content.

Much better efficiency was shown by carbon fillers, when composites were prepared through latex blending. To allow easy dispersion in rubber latex, sp^2 carbon allotropes were functionalized with a serinol derivative: 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP) [2, 3], shown in Figure 1.



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A preliminary in vivo evaluation of CaCO₃ nanocrystals for drug delivery

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A large variety of nano/microparticles has been described in literature and optimised to increase efficacy and sustain the targeting into cancer cells. In our previous work we demonstrated that CaCO₃ microparticles are considered as the ideal drug carriers due to their excellent biocompatibility and ability to readily penetrate cancer cells [1-3]. Here, we propose the synthesis of pure and stable CaCO₃ nanoparticles by spray drying technique and we evaluate the mechanism of cellular uptake, intracellular trafficking and cytotoxicity in two model cancer cell lines, MCF7 and HeLa cells [4]. We exploited the features of this nanomaterial to use it in biological application as vessels of two promising anti-cancer molecules (cisplatin and BEZ-235) [5, 6]. Furthermore, as reported in several studies, the *Drosophila Melanogaster* was used as a model system to learn the detriment caused by nanoparticles. Here, a preliminary effect of oral intake of CaCO₃ nanoparticles were investigated on growth, development and behavior of *Drosophila* because of the high degree of conservation between this animal and mammals with respect to the signaling pathways that control intestinal development, regeneration and disease.

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Self-Assembled Bio-Reducible Hybrid Supraparticles

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In last decades research in the field of nanomedicine received an incredible boost due to the development of nanostructures combining diagnostic and therapeutic abilities in one single object, i.e. theranostic nanoparticles (NPs).¹ However, the potential clinical application of theranostic NPs is often hampered by the complex chemistry involved in their synthesis as well as their low rate of accumulation in the region of interest (ROI) by systemic administration. Self-assembly of small NPs into theranostic Supraparticles (SP)² represents a promising approach to overcome these issues allowing a simplified synthetic procedure, which blends more NPs in one single nano-object able to deliver a higher number of NPs to the ROI. In this contribution, we present the development of bio-reducible protein assembled SPs composed of small Au-NPs capped with organic ligands, which could also be loaded with hydrophobic drugs. The assembled SPs were stable in physiological conditions for months and were endowed with antifouling properties and an appreciable tumortropic fate. In particular, in vitro studies showed that once these SPs entered the cell, their protein shell was progressively dismantled enabling a controlled release of their cargo. Thus, the assembly of NPs into SPs allowed simultaneous delivery of high Au-NP contents (providing nearly three times greater X-ray attenuation per unit weight than iodine) and drugs to the ROI. Overall, the newly developed SPs represent a promising innovative theranostic system.

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Engineered NanoDrugs for the Treatment of Parkinson Disease

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Parkinson's disease (PD) is one of the major progressive neurological disorders and it affects about 1% of the population over 60 years [1]. Currently, PD is mainly treated with dopamine or L-DOPA, but although this approach alleviates the symptoms it does not cure the disease. On the other hand, therapies based on neuroprotection (through antioxidant molecules) are able to reduce the severity of the pathology.

We already demonstrated that highly biocompatible fluorescent NPs could be engineered with a dopamine prodrug and a galactose vector to allow specific targeting and selective delivery [2]. We now synthesized polymeric NPs for the sustained delivery of dopamine and other antioxidant drugs that may be useful for the treatment of Parkinson Disease (PD) [3]. Furthermore, functionalization of the NPs surface with galactose could help to cross the Blood Brain Barrier (BBB), which is a mayor limiting factor the in current drug delivery therapies. The delivery of dopamine and other natural antioxidant molecules reduced significantly the oxidative stress of SHSY-5Y cells in *in vitro* experiments by reducing ROS production. The prepared NPs also showed to be non-cytotoxic at the employed concentrations and could be potentially used as engineered nanocarriers for the selective combined delivery of dopamine and other antioxidants in the PD treatment after further studies will be carried out.

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Aerobic Oxidation catalyzed by N-hydroxy compounds: New frontiers in industrial and biological applications

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Alkyl C-H bond activation via hydrogen atom transfer (HAT) processes has lived a new incredible renaissance in the last two decades, representing an important route for the synthesis of high added value molecules and materials¹. In this context, N-hydroxyphthalimide (NHPI) or more in general N-hydroxy compounds homogeneous catalysis has found a starring role and has been particularly exploited for promoting the aerobic oxidation of different organic substrates ^{2,3}. The corresponding N-oxyl radicals, derived from the abstraction of the hydrogen by N-hydroxy group, are the active species of the catalytic cycle. N-oxyl radical is able to abstract hydrogen from hydrocarbons in order to form carbon centered radical that under aerobic condition, reacts with oxygen and forms peroxy radicals. The latter are converted to the corresponding hydroperoxides by the N-hydroxy derivatives, which behave also as good hydrogen donors⁴. In this context, the OH bond dissociation energy (BDE) of the N-hydroxy group plays a crucial role in order to guarantee the high selectivity of the process. In this context, preliminary computational screening was performed in order to provide information about OH BDE and transition state (TS) in the hydrogen abstraction. Two different new families of organo-catalysts were found and their catalytic efficiency was tested in industrial and biological applications. The high solubility of these new catalysts in lipophilic mediums allowed to conduct these catalytic oxidation under solvent-free conditions for the first time. The high catalytic efficiency of N-hydroxy derivatives in promoting oxidative processes, suggested us a possible alternative use as pro-oxidants for biological applications, namely the promotion of oxidative stress in cancer cells⁵.

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New solid SERS substrates in bioanalytics

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Surface Enhanced Raman Spectroscopy (SERS) has proven to be a promising technique for biomedical application, such as in the field of cancer diagnosis, provided its sensitivity to analytes at low concentrations in biofluids [1, 2]. The missing link between the analytical method and its clinical application stands in the development of suitable, efficient, cheap and durable plasmonic materials for SERS analysis. Recently, an easy-to-prepare point-of-care tool has been developed in our group based on citrate-reduced silver nanoparticles dip-coated filter paper sheets [3], suitable for portable Raman instruments. These substrates revealed a high SERS sensitivity for biological applications. Moreover, the optimization of the experimental set-up for these kinds of SERS measurements is required, considering the necessity of reproducible data. In this frame, the role of protein corona formation around the metal nanoparticles has yet to be unraveled, since it limits the analyte-nanostructures interaction required for the signal amplification. In this work, a systematic study is presented on how the presence of human serum albumin, one of the most abundant proteins in serum, can affect the free diffusion of small molecular weight analytes toward the metal nanostructured surface and their adsorption on it, by means of SERS of model solutions. The adsorption kinetics of known biomolecules on silver solid substrates has been studied by means of simple model systems (single or mixed solute solutions of adenine, hypoxanthine, uric acid, human serum albumin - HSA). This systematic analysis has provided information about the binding constants and the adsorption rate on solid SERS substrates. This may be helpful in the peak assignment of SERS spectra of complex biofluids. Moreover, the possibility to perform quantitative analysis by means of SERS spectra has been assessed on the in-house developed paper-based solid substrates.

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Humidity/temperature sensing cotton fabric based on MWCNTs hybrid coating

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Carbon nanotubes (CNTs) have attracted the interest of the scientific research in several fields thanks to their intrinsic chemical-physical properties [1] and their cylindrical structure that make them, furthermore, capable of molecular transport. Thanks to their electrical properties, CNTs can be used in sensoristic and electronic fields, but at the same time, they can be considered as a viable alternative to traditional conductive inorganic materials. Indeed, CNTs are able to detect variations in environmental chemical composition [2] or toxic gas molecules at room temperature, and they can be employed for the realization of electric circuit for flexible and wearable electronics. Recently, the demand for conductive fabrics is increased both for the realization of "technical fabrics" [3] and "smart textiles" which provide applications in different fields such as sports, healthcare, military, security and so on. With the aim to combine the sensing and electronic features of CNTs with mechanical characteristics of a fabric, a humidity/temperature sensor cotton fabric based on a conductive coating containing Multi Walled Carbon Nanotubes (MWCNTs) dispersed in a polymer matrix has been designed. The realized MWCNTs-cotton based sensor was fully investigated by different chemical-physical techniques in order to evaluate the morphology of the coating. Sensing properties were studied by measuring changing in the surface resistance (R_{sheet}) at different relative humidity and temperature conditions. In particular, R_{sheet} seems to be influenced by water molecules that interact with MWCNTs connections. Experimental findings demonstrated the sensing properties of the realized MWCNTs coating toward humidity and temperature and its potential employment as a component for a humidity/temperature sensor.

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Engineering functional skeletal muscle networks by tailoring matrix stiffness and geometrical confinement

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Skeletal muscle can self-repair relatively small damages resulting from tears, small lacerations, strains, or toxins via a three-stage process that involves demolition, repair, and remodeling of myotubes. However, skeletal muscle cannot restore significant tissue loss that can arise after severe trauma, invasive surgeries, or degenerative diseases. 3D bioprinting has the potential to fabricate highly customizable and highly organized structures that, in principle, could be used for the assembly of an entire muscle [1]. Inspired by the native structural morphology of skeletal muscles, we speculated that the spatial confinement of muscle precursor cells (C2C12) into highly aligned and compact 3D bioprinted hydrogel fiber structures could lead to a better orientation of the arising myotubes, thus mimicking the natural muscle morphology and organization more closely [2,3]. Building on such a premise, we developed a 3D bioprinting strategy based on a custom microfluidic printing head coupled to a co-axial extruder for the high-resolution deposition of multi-material and multi-cellular structures. Within few days of in vitro culture following 3D bioprinting, C2C12 started to elongate and fuse, forming highly aligned myotubes. The obtained myo-structures were thoroughly analyzed in terms of myotube length and orientation, fluorescence immunocytochemistry, and gene expression of relevant myogenic differentiation markers, revealing a significant differentiation and maturation of myotubes. These studies have the potential to unveil the mechanisms by which muscle precursors sense substrate stiffness and confinement, therefore representing a key starting point for the development of novel skeletal muscle regeneration strategies.

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POSTER

Lignin-based nanofillers for bio-based thermoplastic polymer nanocomposites

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Lignin is a naturally occurring aromatic polymer found in the plant cell wall. Despite the large availability of lignin on Earth, it is still enormously underutilized at industrial scale, as its fate is typically to be burnt as low-cost fuel for energy generation. The large number of functional groups present in lignin (e.g., aliphatic and aromatic hydroxyls, carbonyls, carboxyls) makes this material particularly attractive as reinforcing filler for the preparation of polymer-based composites, due to the potentially favourable covalent and non-covalent interactions that may arise between such highly-functional filler and the polymeric matrix. Different attempts have been made involving the incorporation of lignin particles (generally in the 10-100 μm range) into plastics and rubbers. A straightforward addition of lignin into the target matrix unfortunately yielded little or no effect on the mechanical response of the so-obtained composite. Instead, the use of lignin-based nanoparticles (LNP) is an alternative strategy aiming to achieve an enhanced dispersion level of lignin filler within the polymer matrix. Indeed, LNP are expected to provide a more efficient interaction with the polymer matrix compared with the micrometer-sized counterpart owing to their larger surface-to-volume ratio thus ultimately resulting in improved mechanical response of the LNP-based polymer composite material.^[1,2]

In this work, LNP were prepared by ultrasonic treatment of technical softwood kraft lignin to obtain lignin-water dispersions with excellent colloidal stability. A thorough characterization was carried out and a comparison with the parent untreated material was performed. Such LNP were incorporated into a waterborne thermoplastic polyurethane matrix at different concentrations to yield bio-based nanocomposite materials. The bio-filler type effect (LNP vs. untreated lignin), and the concentration on the chemical-physical, thermal and morphological characteristics of the resulting nanocomposites were investigated and the reinforcing effect was discussed based on mechanical tests. The results of this study give a direct demonstration of a viable environmentally friendly approach to obtain waterborne polyurethane-based nanocomposites reinforced with LNP in a straightforward and accessible way and provide clear evidence of the potential of LNP as fully bio-derived fillers for advanced nanocomposite applications.

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Investigations on activating solutions from waste and by-products treatment for geopolymerization

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Sodium silicate solutions (molar ratio, MR, $\text{SiO}_2/\text{Na}_2\text{O}=2-3.3$) used for geopolymerization are generally produced in high temperature and pressure conditions by direct fusion of pure silica sand and soda ash or by hydrothermal process with high energy consumption and environmental impact.

The aim of this work is to synthesize sodium silicate solutions with $\text{MR}=2-3.3$ by means of a low-impacting alkaline treatment of waste glasses (pre- and post-consumer) and rice husk ash (RHA). The treatment conditions are the following: NaOH concentration=1-4 M; contact time= 1.5-3-5 hours; temperature=80-100°C; solid/liquid weigh ratio=1:5; solid particle size <180 and <63 μm ; atmospheric pressure. The stirring effect was also evaluated.

The solutions obtained after filtration were characterized using volumetric titrations based on ISO 1692:1976 and ISO 2124:1972, for the determination of alkali (expressed as Na_2O) and silica (SiO_2).

Results showed that the stirring conditions has a positive effect in terms of extracted silica, since it allowed to continuously renew the solid surface exposed to the alkaline attack.

It was further observed that SiO_2 extraction increased with NaOH concentration. Anyway, in terms of $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, the best results were achieved when NaOH concentration was kept between 1.5-3 M for glass treatment and between 1-2 M for RHA treatment-

The best contact time resulted 3 hours (the increase at 5 hours did not enhance the results).

Compared to waste glasses, RHA was more reactive towards NaOH solution. RHA treatment with NaOH concentration=1-1.5 M and contact time= 3 hours were found to be the best conditions to reach a MR close to 3, ideal for geopolymerization.

The MR reached for waste glasses are instead between 0.17-0.77, too low for geopolymerization, but exploitable for other applications, such as the detergents production and deflocculant solutions.

This study demonstrates that the use of sodium silicate solutions obtained from low-impacting treatment of RHA is promising for the formulation of geopolymers. Besides, considering the high reactivity of RHA, we are investigating further operating conditions at $T=\text{room}$ and at longer time of reaction.

Charge separation at organic photovoltaic interfaces: a coarse-grained quantum chemical view

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Organic semiconducting materials are finding increasing applications in devices such as field effect transistors, light emitting diodes and photovoltaic cells¹. Several fundamental problems in the physics of these materials are still being intensively investigated. One of these is the "localized versus delocalized" nature of their charge carrier and excitonic states². The answer to this question may depend on the specific material and on the degree of thermal or structural disorder, as well as the experimental method used to probe these states. We have addressed this problem by developing an effective quantum chemical model, whereby each molecule is represented by one site with one doubly occupied HOMO and one empty LUMO orbital (in the ground state). Our mesoscale quantum-chemical model³ allows an unbiased assessment of their relative importance, through excited-state calculations on systems containing thousands of donor and acceptor sites. The results on several model heterojunctions confirm that the classical model severely overestimates the binding energy of an electron-hole pair. Using physically sensible parameters for the individual materials, we find that the quantum mechanical energy difference between the lowest interfacial charge transfer states and the fully separated electron and hole is of the order of the thermal energy.

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Biosynthesis of injectable peptide hydrogels for biotechnological applications

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The applications of peptide-based hydrogels are expanding, especially in the biomedical field. These materials in fact possess key features like biocompatibility, biodegradability and ability to assemble into ordered secondary structures. To date, the use of different enzymes, such as proteases, phosphatases and esterases, for the preparation of peptide hydrogels has been reported. In this framework our group has investigated the use of lipolytic enzymes for the preparation of Fmoc-protected peptide hydrogels [1]. The reaction products spontaneously self-assemble in water to originate fibrils, that become entangled to form a three-dimensional structure of fibers with a diameter of approximately 7 nm (Fig. 1). By acting on the chirality and crosslinking degree of the peptides, we were able to tune the morphological and mechanical properties of the hydrogels [2, 3]. These materials can serve as a platform for drug loading and controlled delivery [3]. Our results suggest the possibility of using Fmoc oligopeptides as building blocks for a new class of injectable scaffolds that could play an important role in tissue regeneration applications.

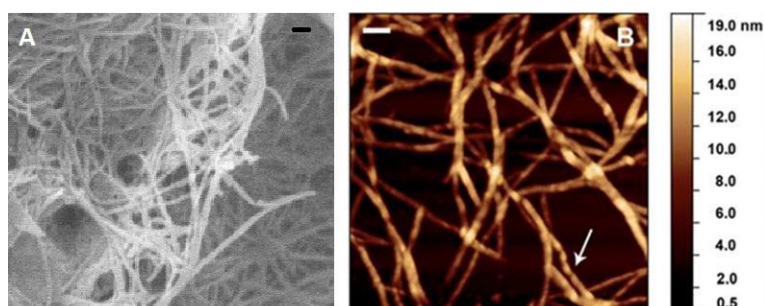


Figure 1- SEM (A) and AFM (B) micrographs of FmocPhe3 hydrogel. Scale bars = 100 nm.

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Multienzymatic and Stereoselective preparation of 2,3-Disubstituted Tetrahydrofurans: The Roasted Meat Aroma Synthesis

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Enantiopure 2-methyl-3-substituted tetrahydrofurans are key synthons for the production of several biologically active molecules such as drugs, flavors, and agrochemicals. Thus, a stereocontrolled and efficient methodology for the obtainment of these products is highly desirable but still challenging. Herein is reported the use of ene-reductases and alcohol dehydrogenases in a two-step multienzymatic cascade reaction⁽¹⁾ for the stereoselective reduction of different α -bromo- α,β -unsaturated ketones to the corresponding bromohydrins. The final products are further manipulated following two diastereodivergent routes: the first based on a lipase catalyzed cleavage of the protecting group; the second characterized by a camphor sulfonic acid mediated isomerization of a β -hydroxyepoxide to give the tetrahydrofuran-2-ol. Both the routes allowed the preparation of different tetrahydrofuranic synthons. One of these is finally used for synthesis of the most odorous and pleasant stereoisomer of the roasted meat aroma, *i.e.*, (2S,3R)-2-methyl-3-thioacetate tetrahydrofuran⁽²⁾.

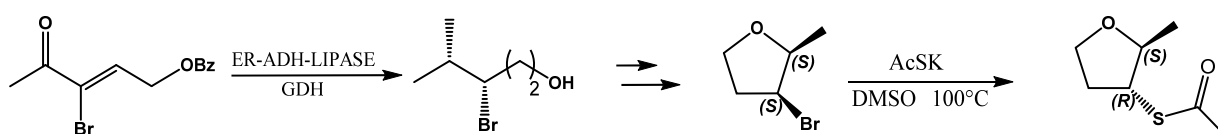


Figure 1: synthetic route for the preparation of the most pleasant stereoisomer of roasted meat aroma.

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Membrane-based crystallization of biomolecules

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Crystallization of biomolecules is a cost-effective technique that can potentially play a crucial role in downstream processing of pharmaceutical active ingredients (API), including proteins.

In this field, membrane-based crystallization is today recognized as a promising method for the production of API with controlled shape, size distribution and polymorphic form. Extension to monoclonal antibodies (mAbs) purification as substitute for a chromatographic (Protein A) process step is today under investigation [1].

According to this innovative technology, membranes are used: (i) to promote mass transfer for a better control of supersaturation (the driving force for crystallization); (ii) to activate heterogeneous nucleation by decreasing the Gibbs free energy barrier to the formation of critical nuclei [2,3].

The impact of physico-chemical properties of microporous hydrophobic polymeric membranes on the nucleation rate of HEW Lysozyme and other protein models, the evidence of polymorphic selection of amino acids and biological molecules as a function of process parameters, and the ability to promote specific intermolecular interactions inducing preferred spatial orientations of solute molecules in proximity of polymeric films are presented.

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Molecularly Imprinted Solid Phase Extraction as a novel approach for radiopharmaceutical products purification

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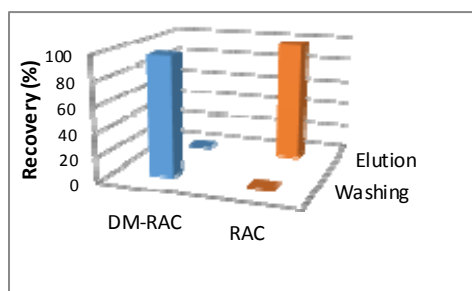
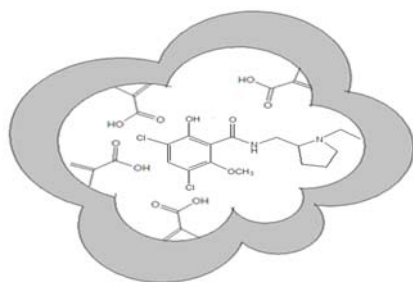
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Radiopharmaceuticals used in Positron Emission Tomography (PET) are produced in very high molar activities, meaning that the chemical mass of the active ingredient is in the low trace range; for this reason, the purification process is a critical step that needs to be achieved in timings compatible with the short half-life of the employed nuclide (e.g. $t_{1/2}(^{11}\text{C})$: 20 min). The traditional separation methods employed involves the use of preparative reverse-phase chromatography. Therefore, the development of a fast, simple and selective purification technique is an important goal. In this respect, Molecular Imprinting Technology (MIT) is a viable synthetic approach to design highly selective molecular recognition elements able to specifically recognize a target molecule.

In this study, MIT applied to Solid Phase Extraction (MISPE), was investigated to develop a device able to selectively extract a specific radiotracer, [^{11}C]Raclopride (RAC) in a mixture containing high amount of its precursor, (S)-O-Des-Methyl-Raclopride (DM-RAC).



To prepare Molecularly Imprinted Polymer (MIP), a thermal polymerization using unlabeled RAC as template was conducted. After several washing to remove the template, the polymer obtained was characterized and packed in empty SPE cartridges. The cartridge was conditioned using acidic conditions and then loaded with one milliliter of a mixture of RAC and DM-RAC. During the washing steps more than 95% of DM-RAC was removed, while no RAC breakthrough was detected. Then, to facilitate the elution of RAC, a basic solution was used and finally about 97% of pure RAC was recovered in injectable-grade formulation. The innovative features of these polymeric materials may help to obtain a successful outcome that allows a faster, simpler and more repeatable overall radiopharmaceutical production.

Synthesis of $Fe_3O_4@SiO_2$ -DFO Nanoparticles for Lanthanide(III) recovery

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Lanthanides (Ln) are employed in many applications (medicine, bio-chemical analysis, catalysis...) and in high-tech materials (magnets, electronics, lasers, OLED...). Unfortunately, they suffer from a high supply risk and are hardly replaceable in many cases.¹ Moreover, many publications evidence its negative effects in living organisms, including humans.² Thus, Ln recovery and recycling would be desirable.

Functionalized magnetic nanoparticles (MNP) are well-suited for the selective extraction of metal ions from diluted wastewater streams or industrial effluents. This is done by capturing metal ions in solution, retrieving the loaded MNP with a magnet and stripping the metal ions from them. This is a sustainable process since the MNP are reusable and there are no hazardous chemicals involved.³

In this work, the synthesis and characterisation of silica-coated MNP functionalized with deferoxamine (DFO) have been carried out. The choice of this natural ligand is related to its good affinity for Ln(III) ions (pK_{LnDFO} 12-18).⁴ The synthesis of this new DFO-MNP has been carried out on the basis of published procedures.^{5,6} The resulting DFO-MNPs have been characterized by TEM, XRD, FTIR, BET, TGA and Elemental Analysis. Adsorption studies on selected Ln(III) ions have been carried out and the samples have been analysed by ICP-OES.

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Synthesis of pyrrole derivatives of serinol for functionalization of carbon allotropes

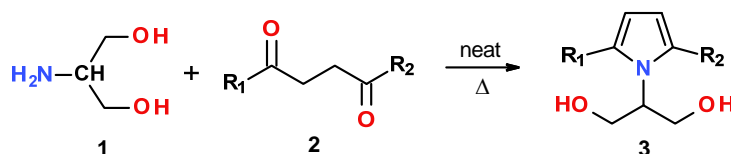
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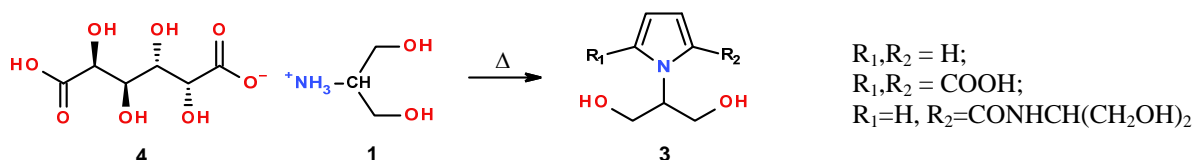
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N-Pyrrole-based heterocycles are present in many natural products,[1] medicinal agents,[2] and functional materials,[3,4] therefore substantial attention has been paid to develop efficient methods for pyrroles synthesis. Moreover, they are precursors for the synthesis of poly *N*-alkyl pyrroles which have wide ranging applications in electronics and sensors due to their tunable optoelectronic properties.

We present here one operationally simple, practical and economical Paal-Knorr pyrrole condensation of serinol (2-amino-propan-1,3-diol, **1**) with beta-dicarbonyl compounds **2** (and related acetal/ketals or enolesters), under neat conditions in the absence of any catalysts, which allows the synthesis of *N*-serinopyrrole derivatives (**3**) in good to excellent yield.



Depending on substituents, compounds **3** show quite interesting amphiphilic polar/unpolar and variable π -interaction properties. The mechanistic conclusion reached in the study, allowed to identify a direct method for the preparation of the precursor serinol-pyrrole from sugar derivatives. Typical examples of this reaction is the dehydrative condensation of galactaric acid (**4**) with serinol (**1**) (i.e. its serinol salt or other derivatives).



Methods for the derivatization of carbon allotropes (CNT, Graphenes and Carbon Black) by the prepared pyrroles were investigated and the good dispersion properties of the resulting material proved.

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BMIm Acetate as Carbene Source: an Electrochemical Evidence

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N-Heterocyclic carbenes (NHCs) are important molecules in organic chemistry, as they are used as ligands for transition metals, organocatalysts, catalysts in metal-free synthesis of polymers, etc. They are obtained by deprotonation of a suitable azolium salt, due to the relative acidity of the C2-H group of the cations. This deprotonation can be carried out by a base or by electrochemical reduction of the C2-H bond.¹ NHCs are usually unstable and thus they are generated in situ.

Recently it was reported that acetate anion could be a base strong enough to deprotonate the azolium cation in the 2-position, yielding the corresponding NHC. Despite the fact that no direct evidence of NHC presence in azolium acetate ionic liquid was gained, NHC catalyzed reactions (e.g., benzoin condensation²) were carried out in the presence of azolium acetate without the intervention of a base. Moreover, quantum chemical calculations ruled out the presence of NHC in 1-butyl-3-methylimidazolium acetate (BMIm-Ac) and suggested that its reactivity is due to a concerted mechanism.³

Cyclic voltammetry can easily ascertain the presence of NHC in neat BMIm-Ac or in solution, checking the presence of NHC oxidation current at a potential of about 0.5V vs SCE.⁴

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Amino- and guanidinoglycoside based vectors for cell transfection

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The development of efficient alternatives to viral vectors is a hot subject for the uptake of high molecular weight biomolecules like peptides, proteins and genes that can't spontaneously cross the cell membrane. Aminoglycosides, such as neomycin are a class of naturally occurring antibiotics while guanidinoglycosides, such as guanidinoneomycin are aminoglycosides where all the amino groups are converted into guanidino groups. The group of Prof. Tor has shown that guanidinoglycosides are very efficient molecular transporters facilitating the intracellular delivery of high molecular weight cargos at nanomolar concentrations by binding selectively cell surface heparan sulfate proteoglycans¹.

Recently, our group has been involved in the synthesis of aminoglycoside and guanidinoglycoside-based vectors for an efficient gene and drug delivery^{2,3}. Since then different carriers have been developed including cationic lipids systems (using calix[4]arenes and cyanuric chloride as scaffolds) and colloids such as PEG-PEI nanogels decorated with GNeo. The synthetic part along with biological tests on cell viability and transfection efficiency will be reported.

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Anisotropic diffusion in PEO-LiTFSI-Pyr₁₄TFSI ternary systems: ¹H microimaging NMR study.

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Ternary electrolyte systems obtained from ionic liquid (IL) N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI), polyethylene oxide film (PEO) and LiTFSI has attracted interest for the potential use as polymer electrolyte in lithium ion batteries [1]. Magnetic resonance imaging (MRI) of small samples with high resolution on the order of 10 μm (μMRI, MR microimaging) is used as excellent tool for non-invasive investigations of the diffusion processes in material science and medicine. The NMR probe is equipped with field gradients along x, y and z axes, thus allowing the measurement of the diffusion coefficients in arbitrary spatial direction. Samples with variable IL concentration (components molar ratio (PEO-LiTFSI-Pyr₁₄TFSI) 20/2/x x=0,2,4,6,8) were prepared and observed. The diffusion-weighted images of section of PEO membranes coiled along the axial direction provide a clear picture of the anisotropic motions of the Pyr₁₄ cation within the membrane. The result clearly indicates that the cation exhibits not only different diffusion coefficients in different positions of the ternary system, but also that the diffusion motion in the x and y directions is hindered: $D_z > D_x = D_y$. The observation of macroscopic diffusion anisotropy is a result of an underlying ordered microstructural organization of IL components in polymeric materials.

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Aerogels of enzymatically oxidized galactomannans: versatile delivery systems of antimicrobial compounds and enzymes

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Galactomannans (GM) are high molecular weight polysaccharides found in the seed endosperms of some *Leguminosae* (belonging to the family *Fabaceae*). They have a branched polymeric structure composed of a backbone of mannose units linked by B-1,4 glycosidic bonds with side units of galactose bound to mannose by a α -1,6 glycosidic bond. The average ratio of galactose to mannose (Gal: Man) is variable, depending on the plant species.^[1] GM derivatives are produced on an industrial scale and are employed as rheology modifiers, thickening and suspending agents in food, feed and industry.

Laccase/TEMPO oxidation of GM leads to structured, elastic, stable hydrogels. This due to formation of carbonyl groups from primary OH of galactose side units and subsequent establishment of hemiacetalic bonds with available free hydroxyl groups. Upon lyophilization of these hydrogels, water-insoluble aerogels were obtained, capable of uptaking aqueous or organic solvents several times their own weight. These materials were characterized by scanning electron microscopy, FT-IR, elemental analysis and ¹³C CP-MAS NMR spectroscopy, the thermal and mechanical properties, and porosity were investigated.^[2,3] To test these new materials as delivery systems, the following model actives were absorbed into GM aerogels from aqueous solutions: the chemical biocides; the antibiotic; the antimicrobial peptide; the enzymes lysozyme, protease and lipase.^[4]

We suggest that aerogels made from enzymatically oxidized and lyophilized GM from leguminous plants, could represent very innovative, versatile, biocompatible delivery systems of various active principles, with potential applications in the biomedical field, as well as in food packaging, feed and industrial products.

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Truxene-based Hole Transporting Materials for Perovskite Solar Cells: Direct vs Inverted Configuration Devices

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Organic-inorganic lead halide perovskites have rapidly become one of the hottest topic in photovoltaics. Their use requires the presence, in devices, of hole-transporting materials (HTMs) to extract the photo-generated holes from the perovskite, and transport them to the electrode.¹ The molecular tailoring of HTM for perovskite solar cells, however, still lacks in solid design criteria.² Aiming at providing guidelines in this field, in marked contrast with the 3-D structure of the *state-of-the-art* Spiro-OMeTAD, truxene-based HTMs **Trux1** and **Trux2** have been employed for the first time in PSCs fabricated with a direct (n-i-p) or inverted (p-i-n) architecture, exhibiting a peculiar behavior with respect to the referential HTM. Notwithstanding the efficient hole extraction from the perovskite layer exhibited by **Trux1** and **Trux2** in direct configuration devices, their photovoltaic performances were detrimentally affected by their poor hole transport. Conversely, a remarkable improvement of the photovoltaic performances in dopant-free inverted configuration devices compared to Spiro-OMeTAD (13,4% respect to 9,5% for **Trux2** and Spiro-OMeTAD respectively) was recorded, ascribable to the use of thinner HTM layers. The rationalization of the photovoltaic performances exhibited by different configuration devices can provide new and unexpected prospects for engineering the interface between the active layer of perovskite-based solar cells and the hole transporting material.

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Calcium alginate: a powerful tool in technological up-grade for biocatalytic reactions.

Immobilization of Acetobacter aceti in 1,3-diols oxidation.

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Biocatalysis has reached in the past decades great interest, above all in pharmaceutical field, where great efforts are employed in the synthetical strategy. As a case study, it is reported the biocatalytic synthesis of enantiomerically enriched hydroxymethyl alkanolic acids, interesting intermediates in the synthesis of α -substituted- β -lactones (possible ClpP inhibitors). The microorganism *Acetobacter aceti* was selected as a valuable biocatalyst for the enantioselective desymmetrization of achiral 2-substituted-1,3-diols to the corresponding hydroxymethyl alkanolic acids¹. By investigating the oxidative potential on a set of 2-substituted-1,3-propandiols, additional side-reactions were observed, leading to the formation of the corresponding α -methylenic and α -methyl alkanolic acids². In order to determine a technological improvement, it was decided to immobilize bacteria cells by entrapment inside a polymeric matrix. Alginate was chosen for its easily employment as a gel: being soluble in water as sodium salt, and insoluble as a gel in presence of bi- or tri- valent cations, beads of calcium alginate can be obtained by ionic exchange between sodium and calcium³. The diol oxidations showing side products were tested with immobilized cells affording good results both for selectivity and conversion. As a further up-grade, tests under continuous-flow conditions were performed. The increased productivity shown by using this technology has been considered of interest for future works by determining the best conditions for process intensification.

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On the morphological, structural and charge transfer properties of F-doped ZnO: a spectroscopic investigation

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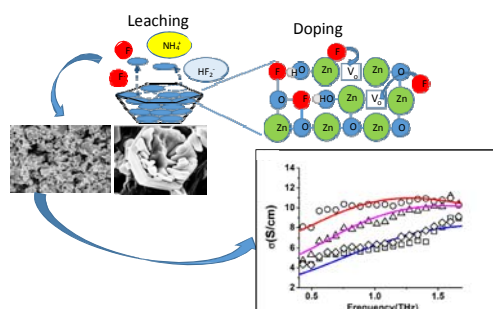
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Zinc oxide (ZnO) is a versatile semiconductor extensively used in different technological applications. Different kind of doping have been applied to ZnO, aiming at improving conducting properties but preserving its transparency. In this



work, we have prepared F-doped ZnO powders through hydrothermal synthesis and characterized by different spectroscopic techniques in order to discern the effective capability of F atoms to improve ZnO conductivity [1]. Experimental results show that F atoms do not work as donors but rather

affect the morphology of ZnO crystals, promoting the onset of a granular phase. X-Ray Diffraction (XRD) analysis indicates that F doping does not change crystallographic components of ZnO powders up to 5 at.% concentration. Photoluminescence (PL) and Electron Paramagnetic Resonance (EPR) spectra proved the effective F doping of ZnO structures, also showing that F atoms mainly occupy oxygen vacancies, inherently present in the undoped ZnO. The increase of luminescence centers revealed via PL data well corresponds to the rise of asymptotic permittivity detected by THz spectroscopy. Indeed, the doping precursor exerts a relevant leaching on ZnO mesocrystals, leading to an increase of the smaller nanoparticles fraction, consequently of scattering rate at grain boundaries, ultimately affecting the conductivity.

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