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SCI is extremely grateful to Vinavil S.p.A for contributing to the sponsorship of this conference

Welcome message

Dear participants,
welcome to the first edition of the **Merck Young Chemists Symposium**, formerly SAYCS.

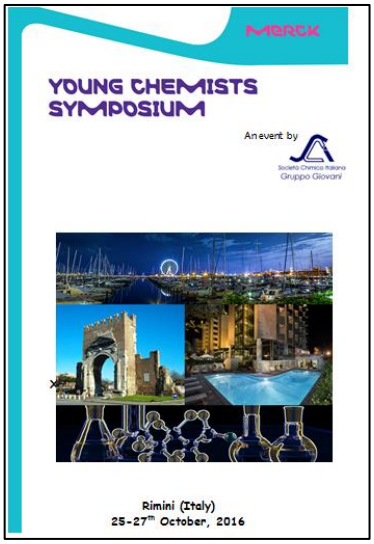
This conference is an international scientific event organized by the Italian Chemical Society (SCI) with the financial support of Merck.

This symposium is fully devoted **to young researchers**, such as MSc and PhD students, post-doc fellows and young researchers in enterprises. All the disciplines of **Chemistry** are covered: analytical, physical, industrial, organic, inorganic, theoretical, pharmaceutical, biological, environmental, macromolecular and electrochemistry. This year, a special emphasis will be given to **ubiquitous chemistry**: *why chemistry is increasingly present in all of the fields that are fundamental for human life, i.e. energy, health and environment?*

This year we have a significant number of 168 participants; we thank you for the great trust shown towards the Young Group of the Italian Chemical Society and Merck.

Enjoy the conference!

HOW TO CITE YOUR WORK



The scientific contributions of this conference are collected in an international volume with ISBN code.

You can cite your work in this way:

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01.30-…	Enjoy Rimini!

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INV-1 Thomas BEIN

INV-2 Guido SARACCO

INV-3 Leonard PRINS

INV-4 Gabriele CRUCIANI

INV-1
Light-induced charge separation in covalent organic frameworks

Thomas Bein

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In this talk, we will explore the opportunities offered by spatially integrating photoactive molecular building blocks into a crystalline lattice based on the paradigm of covalent organic frameworks (COFs), thus creating models for organic bulk heterojunctions. We will address means of controlling the morphology and packing order of COFs through additives [1], in thin films [2], and with spatially locked-in building blocks [3]. We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which showed light-induced charge transfer to an intercalated fullerene acceptor phase [4]. Contrasting this approach, we have recently designed a COF integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network [5]. Due to the great structural diversity and the large degree of morphological precision that can be achieved with COFs, these materials are viewed as intriguing model systems for organic heterojunctions.

[1] M. Calik, T. Sick, M. Dogru, M. Döblinger, S. Datz, H. Budde, A. Hartschuh, F. Auras and T. Bein, *J. Am. Chem. Soc.* **138** (2016) 1234-1239.
[2] D. D. Medina, J. M. Rotter, Y. H. Hu, M. Dogru, V. Werner, F. Auras, J. T. Markiewicz, P. Knochel and T. Bein, *J. Am. Chem. Soc.* **137** (2015) 1016-1019.
[3] L. Ascherl, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras and T. Bein, *Nat. Chem*. **8** (2016) 310-316.
[4] M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chem. Int. Ed*. **52** (2013) 2920-2924.
[5] M. Calik, F. Auras, L. M. Salonen, K. Bader, I. Grill, M. Handloser, D. D. Medina, M. Dogru, F. Lobermann, D. Trauner, A. Hartschuh and T. Bein, *J. Am. Chem. Soc.* **136** (2014) 17802-17807.

INV-2

CO_2 conversion and storage, from lab-scale to industry-scale

Guido Saracco

Center for Sustainable Futures, Istituto Italiano di Tecnologia, Corso Trento 21, 10129-Torino, Italy
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The reduction of CO_2 emissions is now a well defined path at European level far beyond the fateful 20-20-20 agreed in Kyoto. The European roadmap (http://ec.europa.eu/clima/roadmap2050), agreed by European Heads of State in 2014, already expects the achievement of the 40% reduction in CO_2 emissions for 2030 compared to 1990 levels, with a view (well outlined in the chart below) to reach the 80% reduction by 2050. The recent agreements of Paris (December 2015) essentially confirm this perspective, bringing it to be considered at a worldwide level. Indeed, 195 countries have signed these agreements with the aim to keep global warming of the Earth's surface well below 2 °C when compared to pre-industrial period. As clearly shown in the figure and in line with what was stated above, this will have a transversal impact on all sectors of production and service.

It is unrealistic to achieve this result without a radical technological innovation that is based on materials, processes and innovative technologies that, integrated into the intelligent networks management, bring renewable energy to become the core of these areas. Significant technologies that aim not only to the sequestration of CO_2 but also to re-use/conversion through renewable energy to synthesize compounds, materials, fuels alternative to fossil ones, will be pushed by governmental actions and promoted by key stakeholders [1-3]; besides this, the development (already ongoing) of conversion of renewable energy into electricity (photovoltaics, wind, etc.) and the storage of this latter (through lithium and post-lithium batteries) will remain fundamental aspect of the present worldwide scenario.

This presentation provides a comprehensive overview of the international research on the most promising technologies currently in vogue in this area.

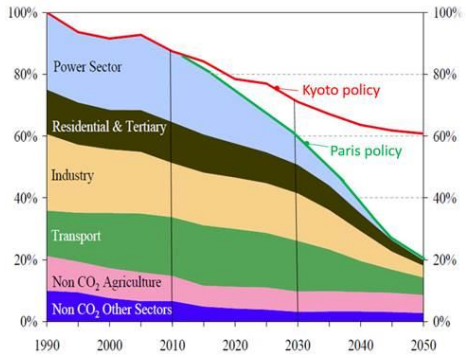

Figure 1: CO_2 emissions reduction planned in Europe.

[1] H. M. Henning and A. Palzer, "The role of power-to-Gas in achieving Germany's climate policy targets with a special focus on concepts for road-based mobility", 2014.
[2] J. De Joode, B. Daniëls, K. Smekens, J. Van Stralen, F. Dalla Longa, K. Schoots, A. Seebregts, L. Grond and J. Holstein, "Exploring the role for power-to-gas in the future Dutch energy system", 2014.
[3] C. Marzano, P. Petrov and S. Bøwadt, "Transforming CO_2 into value for a rejuvenated European economy", 2015.

INV-3
Self-organization and evolution of chemical systems

Leonard J. Prins

Dipartimento di Science Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131-Padova, Italy
E-mail: leonard.prins@unipd.it

Living organisms need energy to stay alive. Translated into terms of chemistry, this implies that life is a kinetically, rather than thermodynamically, stable state. Over the past decades, chemists have mastered the art of assembling small molecules into complex nanostructures using non-covalent interactions. The driving force for self-assembly is thermodynamics: the self-assembled structure is more stable than the separate components (Figure 1a). Such self-assembled structures are now used as functional catalysts, sensors, and materials. However, they differ in a fundamentally different way from natural systems, which are NOT at thermodynamic equilibrium. The challenge is now to develop chemical systems in the laboratory that require energy consumption to maintain their state (Figure 1b). On one hand, such systems may lead to a better understanding of self-assembly in Nature, but may also may lead to innovative catalysts and sensors. Here, we discuss the self-assembly of complex chemical systems under thermodynamic control and out-of-equilibrium and applications in molecular sensing and catalysis [1-3].

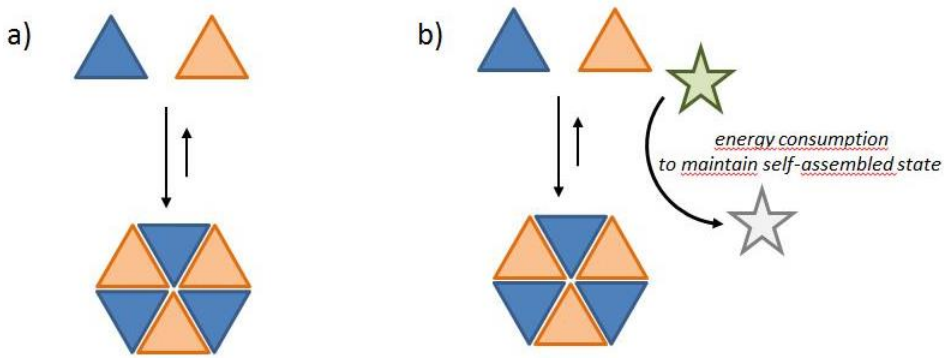

Figure 1: (a) Self-assembly and (b) dissipative self-assembly.

[1] L. J. Prins, *Acc. Chem. Res.* **48** (2015) 1920-1928.
[2] C. Pezzato and L. J. Prins, *Nat. Commun.* **6** (2015) 7790.
[3] S. Maiti, I. Fortunati, C. Ferrante, P. Scrimin and L.J. Prins, *Nat. Chem.* **8** (2016) 725-731.

INV-4
Lipidomic fingerprint for toxic endpoint prediction

Gabriele Cruciani,[a] Simone Sciabola,[b] Robert Stanton[b]

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[b] *Pfizer, Neuroscience and Pain Research Unit (NPRU), Boston, USA*
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Many marketed or under development drugs induce lipid disorders, constituting major risk factors for hepatic injury. Drug-induced lipid disorders are often unpredictable in preclinical stages, and related adverse events have led to post-market withdrawal of drugs. In particular, phospholipidosis (DIPL) and steatosis (DIST) are considered possible alarms for early Drug Induced Liver Injury. Chemical structure-based models for the prediction of liver toxicity have only modest performance, highlighting that there is no simple relationship between chemical features and toxicity. Bioassays for small molecules that assess their cytotoxicity and potential for inducing mitochondrial dysfunction in liver cell lines are routinely run in pharmaceutical companies, however, often profiled known hepatotoxic compounds did not show activity even when tested at high concentrations.

The paper presents the evaluations of the ability of lipidomic fingerprints to predict DILI for a set of well characterized marketed drugs that have also been tested in other bioassays. More precisely, the 3D tissue culture of primary human hepatocytes co-cultured with Kupffer cells will be used. These cells performance are stable up to 14 days in term of basal metabolism and xenobiotic metabolic capability, and they can be drug-treated for long time in sub-chronic conditions. Kupffer cells strongly regulate the hepatocyte functions, therefore their presence in the culture give a model much more similar to the in vivo system. Furthermore, the currently used cell system (HepG2 or HEPARG) express only partially the xenobiotic metabolized enzyme systems. This means that the effects of xenobiotics on lipid metabolism, on these cell cultures, lack the information related to the role of hepatic metabolite(s).

It is shown that any chemically-induced change/modification of a cellular function is reflected in several modifications of lipid content. The lipid profile consists of more than 40,000 different lipid molecules which composition is very sensitive to cellular perturbations, modifications, alterations induced by diseases and/or by pharmacological treatments. Therefore a lipid profile is a fingerprint for adverse effects or potential biomarkers in hepatocyte model to exploit negative (or positive) effects during their first line of therapeutic protocol.

Oral Presentations

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OR-2	Francesca PIAZZOLLA	**OR-30**	Chiara PARISE
OR-3	Thanh Binh MAI	**OR-31**	Fabiola SCISCIONE
OR-4	Riccardo ZENEZINI	**OR-32**	Polyssena RENZI
OR-5	Carlotta GRANCHI	**OR-33**	Gianpiero VALENTE
OR-6	Sergio BOCCHINI	**OR-34**	Cecilia POZZI
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OR-27	Susan LEPRI	**OR-55**	Simona RANALLO
OR-28	Luca LAVAGNA	**OR-56**	Gianluigi ALBANO

OR-1

A modular clamp-like mechanism to regulate the activity of nucleic-acid target-responsive nanoswitches with external activators

Erica Del Grosso,[a] Andrea Idili,[a] Alessandro Porchetta,[a] and Francesco Ricci[a]

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Here we demonstrate a general and modular approach to regulate the activity of target-responsive DNA-based nanoswitches [1]. We do so by coupling together two DNA-based responsive elements: a triplex-forming clamp-like probe able to bind a specific DNA sequence and a split aptamer selected to bind a small molecule. In the presence of the specific target of one of the above responsive elements, the nanoswitch partially folds and its ability to bind the second target is restored. With this approach we can finely modulate the affinity of both DNA-recognition elements and aptamers using an external ligand. The modular nature of our strategy makes it easily generalizable to different DNA based recognition elements. As a demonstration of this we successfully designed five different DNA nanoswitches whose responsiveness can be regulated by different molecular effectors and targets. The convenience with which this mechanism is designed suggests that it may prove a useful tool by which sensors, genetic networks and other biotechnology devices employing nucleic-acid based receptors can be controlled with an external input.

[1] E. Del Grosso, A. Idili, A. Porchetta and F. Ricci, *Nanoscale*, just accepted.

OR-2

Green three-component approach to 2-phenyl-4-acetoxybenzoate derivatives as intermediates in the synthesis of pharmaceuticals

Francesca Piazzolla,[a] Andrea Temperini,[a] and Lucio Minuti[b]

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[b] *Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, 06123-Perugia, Italy*
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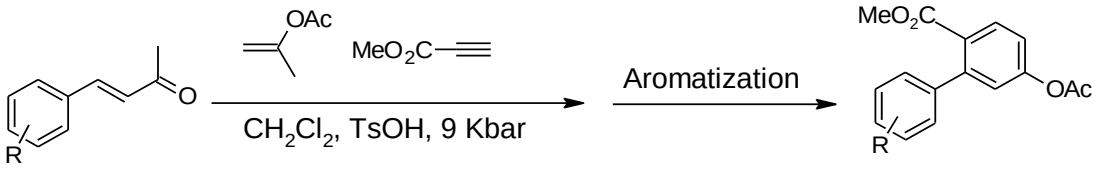
In the last decades, toxicity [1] and environmental issues concerning transition metal catalysts have increased the development of metal-free synthetic strategies to give an alternative access to the usual cross-coupled products.

High-pressure can be considered an environmentally friendly method which has already been used to pursue the synthesis of pharmaceuticals [2].

Herein, we report an efficient three-component metal-free approach to 2-phenyl-4-acetoxybenzoate derivatives based on a high-pressure promoted tandem TsOH catalyzed enolacetylation of variously functionalized 4-phenyl-but-3-en-2-ones and a sequential Diels-Alder reaction of the acetoxydiene generated in situ with methyl propiolate. The adducts were then easily isolated and aromatized.

Provided that the aromatized adducts can be used as intermediates in the synthesis of privileged structures for protein binding [3], studies on pharmaceutical applications of this synthetic strategy are currently ongoing in our laboratories.



[1] EMEA, "Guideline on the specification limits for residues of metal catalysts", 2007.
[2] L. Minuti, A. Temperini and E. Ballerini, *J. Org. Chem.* **77** (2012) 7923-7931.
[3] L. Costantino and D. Barlocco, *Curr. Med. Chem.* **13** (2006) 65-85.

OR-3

OR-4

Identification of endogenous bioactive peptides from donkey milk by multidimensional liquid chromatography and nanoHPLC-MS/MS

Riccardo Zenezini Chiozzi, Anna Laura Capriotti, Francesca Ferraris, Giorgia La Barbera, Susy Piovesana, and Aldo Laganà

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Donkey milk is valuable product for the food industry, and it is nowadays considered a "pharmafood" for its nutraceutical, nutritional and functional properties [1]. Donkey milk strongly resembles human milk because it contains similar amounts of lactose and minerals and similar fatty acid and protein profile; for these reasons it is considered the most suitable mammalian milk for infant consumption, especially in case of cow milk allergy. In the last years interesting biological activities, such as anti-inflammatory, antiallergic, antimicrobial, antioxidant, immunological properties related to the prevention of atherosclerosis, antiviral activity and the antiproliferative effect on A549 human lung cancer cells were ascribed to donkey milk [2]. In this work a combination of consecutive chromatographic separations, including reversed phase liquid chromatography (RP-LC) and hydrophilic interaction chromatography (HILIC), was used to purify endogenous peptides in donkey milk. The most active fractions, with the highest antioxidant (AO) and ACE-inhibitory properties obtained from second chromatographic dimension, were further analyzed by RP nano-HPLC with direct injection into a Orbitrap mass spectrometer for peptide sequencing. *In silico* analysis using Peptide Ranker was then employed to ascribe a bioactivity rank to each peptide. Finally, on the basis on the composition and the probability as calculated by Peptide Ranker algorithm, 5 peptides were selected and synthetized, and their AO and ACE-inhibitory activities were determined by in vitro bioassays. Finally, for further confirmation the synthetized peptides were compared to the natural occurring ones checking their retention times and fragmentation patterns of the five selected peptides in donkey milk alone and donkey milk with spike-in peptides.

[1] I. B. Bidasolo, M. Ramos and J. A. Gomez-Ruiz, *Int. Dairy J.* **24** (2012) 146-152.
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OR-5

Discovery and optimization of new reversible MAGL inhibitors

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Monoacylglycerol lipase (MAGL) is a serine hydrolase that plays a major role in the degradation of 2-arachidonoylglycerol, an endocannabinoid neurotransmitter implicated in several physiological processes [1]. MAGL inhibitors are considered as potential therapeutic agents for a variety of pathological conditions, including several types of cancer. So far only a limited number of MAGL inhibitors have been discovered and most of them are characterized by an irreversible mechanism, thus determining an unwanted chronic MAGL inactivation, which produces a functional desensitization of the endocannabinoid system. However, the application of reversible MAGL inhibitors has not yet been explored, mainly due to the scarcity of known compounds possessing efficient reversible inhibitory activities.

In this study we report the identification of a reversible MAGL inhibitor by a structure-based virtual screening analysis (compound *CL6a*), which showed to be a promising reversible MAGL inhibitor (K_i = 8.6 µM on *h*MAGL) [2]. With the aim of identifying more potent and selective MAGL inhibitors, chemical modifications were made to the structure of the initial compound *CL6a*. Structural optimization of the amidic phenyl fragment led to derivative *11b* (K_i = 0.65 µM on *h*MAGL, Figure 1), which can be considered as one of the most active reversible MAGL inhibitors ever reported so far in the literature. Moreover, this compound was selective for *h*MAGL *versus* the analog enzyme fatty acid amide hydrolase (FAAH) and it produced an appreciable inhibition of cell viability against a panel of cancer cell lines.

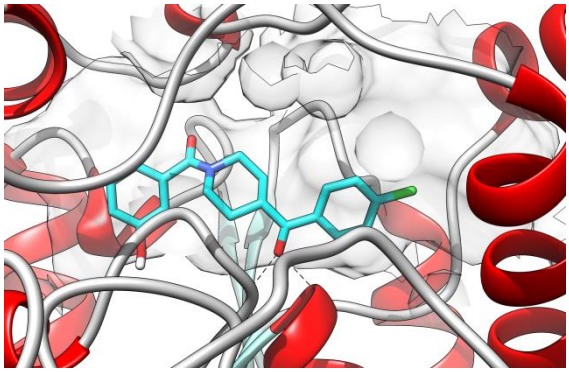

Figure 1: Binding disposition of compound *11b* into *h*MAGL.

[1] M. M. Mulvihill and D. K. Nomura, *Life Sci.* **92** (2013) 492-497.
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OR-6

Facile synthesis of green amino acid based ionic liquids and their use for CO_2 capture

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The development of novel technologies for the efficient and reversible capture of CO_2 is highly desired. In the last decade, CO_2 capture using ionic liquids (ILs) has attracted intensive attention from both academia and industry, and has been recognized as a very promising technology. Recently, a new approach has been developed for highly efficient capture of CO_2 by site-containing ILs through chemical interaction [1]. However, it has emerged that commonly used imidazolium- and pyridinium-based ILs are not as environmentally friendly as previously thought. For instance, such ILs generally showed considerable toxicity to enzymes, microorganisms and cells as well as to whole animals and plants and most could not be considered as 'readily biodegradable'. It has been widely demonstrated that the cations of ILs, especially the head groups, play a major role in toxicity [2]. Choline is a soluble vitamin usually grouped within the 'B-complex vitamins'. The cholinium ion is a promising candidate as ILs cation since the quaternary ammonium cation incorporating a polar hydroxyl group has a relatively low toxicity. Alpha amino acids (AA), the main precursor of proteins, are of low cost, have low environmental impact, high biodegradability, negligible volatility and high biological activity. They are easy to obtain in large quantities at a relatively high purity and can be used as anions. Choline amino acid ILs were prepared for the first time through [OH]-exchange followed by acid–base neutralization [1].

In our work a general simple method to prepare choline-based ILs starting from choline chloride, amino-acids and potassium hydroxide was developed using selective precipitation of potassium chloride in a green solvent such as ethanol. This synthesis has several advantages such as shorter preparation time, very high yields (close to 100%), high reproducibility, and no use of toxic solvents. The chemo-sorption of CO_2 in pure choline-based ILs and their solutions with high boiling low toxicity solvent was studied. The performance of the different ionic liquid results to be highly dependent from viscosity, type of AA used and concentration of functional groups.

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OR-7

Selenium-prenyl containing compounds as drug candidates

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Since its discovered by Jakob Berzelius in 1817, Selenium (Se) was mainly considered a toxic element. Starting from 1957 it was found to be an essential micronutrient, the deficiency of which was correlated with many human diseases (reviewed in [1]). The physiological role of Se came to light when it was found to be a functional component of Se-proteins with key role for instance in the catalytic activity of Se-enzymes. Glutathione peroxidase (GPx) was one of the first selenoproteins discovered in mammals and the most studied one since of the central role in the defense against oxidative stress [2].

This role of Se has stimulated a growing interest on the GPx mimetic function of organoselenium compounds [3]. Thank to our expertise on natural and semi-synthetic *O*-prenyl secondary metabolites, we recently used the scaffold of anthranilic and p-aminobenzoic acids to synthesize a first group of *Se*-prenyl derivatives containing *3,3-dimethylallyl* and *geranyl* side chains (Figure 1). Thiol peroxidase activity of these compounds was investigated according to [4]. Organoselenium compounds were found to oxidize low molecular thiols to disulfides during the reduction of hydrogen peroxide. The reaction can be easily monitored by ^{1}H NMR spectroscopy using Dithiothreitol (DTT^{red}) as thiol substrate according to [5]. In the absence of the synthesized organoselenium catalysts (10 mol %), no appreciable thiol oxidation was observed. Finally the concentration- and time-dependent effect of prenylselenide compounds on viability and ROS generation of HepG2 human hepatocarcinoma cells, was evaluated. Compound D showed the higher cytotoxic activity and along with compounds B and C stimulated ROS production in this cell line. Further studies are in progress to explore the antioxidant and anticancer activity of this novel group of *Se*-prenyl compounds.

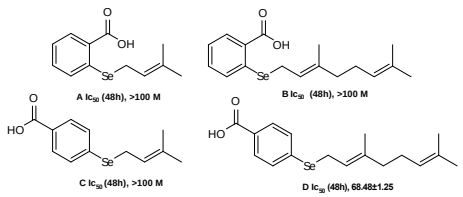

Figure 1: *Se*-prenyl compounds (A-D) under study

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OR-8

A semi-solid lithium redox flow air (O_2) battery

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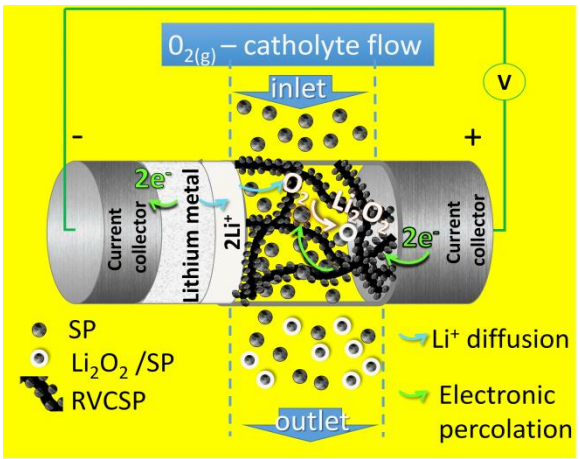
The efficient use of renewable energy sources and a sustainable electric transportation requires high efficiency, energy storage/conversion systems and Li-ion batteries (LIBs) and Redox flow batteries (RFBs) play here a key role. Coupling an O_2-cathode with a lithium anode gives one of the highest performing metal/air chemistry directing towards a next generation of battery. Cathode passivation by discharge products is one of the most serious drawbacks of such batteries, along with the slow O_2 mass transport, which in air breathing cells, limits current densities to one order of magnitude lower than the values for commercial LIBs. To solve these issues, a novel Li/O_2 cell configuration, the Li Redox Flow Air Battery (LRFAB), has been proposed [1]. Replacing solid electrodes with semi-solid slurries has been demonstrated to be an effective strategy to improve battery rate response and we have pursued such approach to demonstrate a new battery concept, a non-aqueous Semi-Solid Lithium Redox Flow Air (O_2) Battery (SLRFAB) that operates with a flowable catholyte [2]. The catholyte is a suspension of conductive carbon in O_2-saturated non-aqueous electrolyte. Oxygen reduction takes place on the semi-solid electroactive dispersed particles, avoiding the electrode passivation, enhancing the Li/O_2 battery capacity and, in turn, the delivered energy. The results of the galvanostatic tests at different currents are here reported as well as the strategies to reach and overcome practical specific energies of 500 Wh kg^{-1} are discussed.



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OR-9

Atropisomeric azaborines first axial chirality about boron-carbon bond

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The first preparation of atropisomeric 2,1-borazaronaphthalenes was recently ahieved [1]. 2,1-borazaronaphthalenes are isosteric molecules of naphthalenes where a C=C bond is replaced by a B-N bond with a substantial modification of the chemical and physical properties. This new class of compounds has attracted much attention over the past few years due to their importance in both medicinal and material science.

X-ray diffraction and Dynamic NMR data allowed the structural and dynamic comparison with the analogue isosteric carbon compounds.

Resolution of the atropisomeric pair was achieved by preparative Chiral Stationary Phase HPLC (CSP-HPLC). The absolute configuration of the stereogenic axis was determined by Time-Dependent DFT (TD-DFT) simulation of the Electronic Circular Dichroism spectra (ECD).

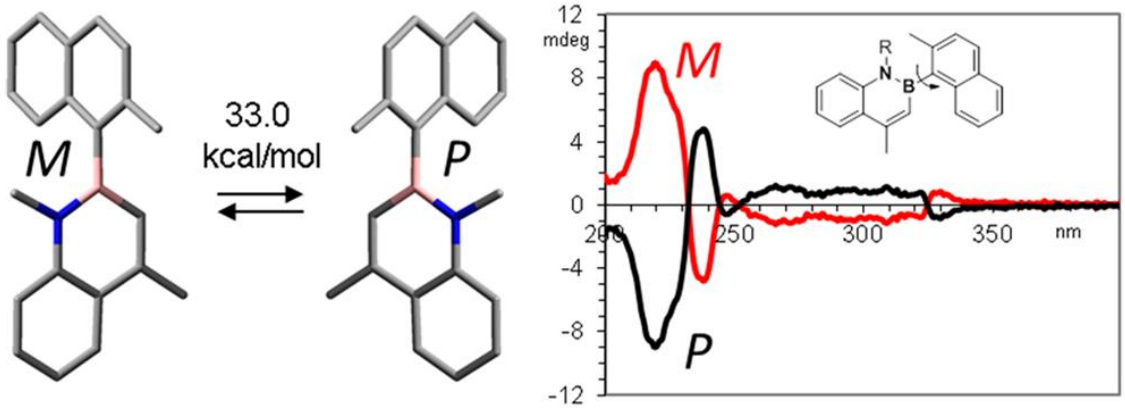

Figure 1: Left: ***M*** and ***P*** configurations. Right: Electronic Circular Dichroism (ECD).

[1] A. Mazzanti, E. Mercanti and M. Mancinelli, *Org. Lett.* **18** (2016) 2692-2695.

OR-10

Dicationic ionic liquids and water mixtures: an insight from theory and experiment

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Ionic liquids (ILs) have been among the most interesting and studied solvents over the past two decades, due to their wide array of possible applications. A new family of "high stability" ILs, geminal dicationic ILs, has been recently developed showing improved properties in terms of stability and efficiency [1]. We have carried out a combined Molecular Dynamics (MD) and extended X-ray absorption fine structure (EXAFS) investigation aimed at disentangling the structural properties of binary mixtures of water and a new class of geminal dicationic IL, namely 1,n-bis[3-methylimidazolium-1-yl] alkane bromide ($[C_n(mim)_2]Br_2$). The synergic use of EXAFS spectroscopy and simulation techniques has become, in the last years, the method of choice to investigate disordered systems allowing one to use accurate structural models for the EXAFS analysis while assessing the reliability of the MD results [2]. The properties of $[C_n(mim)_2]Br_2$/water mixtures have been investigated as a function of both water concentration and alkyl-bridge chain length, and they have been compared with those of the monocationic counterparts. A complex network of interactions among dications, anions and water molecules takes place. The local molecular arrangement around the bromide ions changes with increasing water content (Figure 1), while decreasing the number of carbon atoms in the spacing chain produces increased interactions between dications and anions, with Br^- ions forming a bridge between the two imidazolium rings of the same dication.

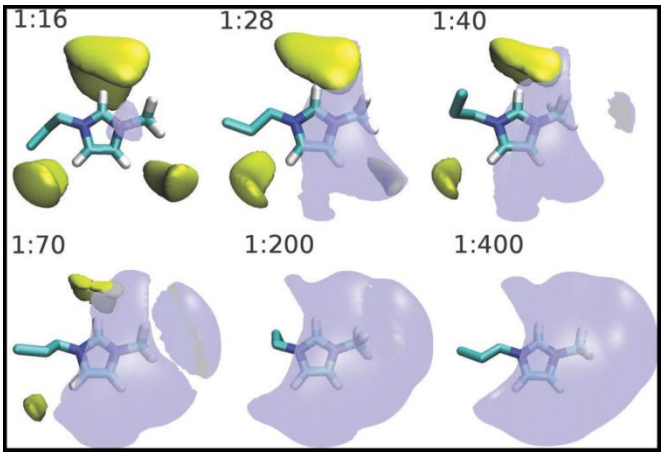

Figure 1: Graphical representation of the spatial distribution of water (blue) and anions (yellow) around one of the two dication rings.

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OR-11
Carbon materials for brake pads

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At present brake pads number a lot of constituents and the "good recipe" is the result of a complex trial and error approach, where the actual contribution from each ingredient is still unknown. With the aim to set up a characterization method devoted to understand the contribution of each ingredient, the authors focus the attention on one of the most widespread material used as friction additive, i.e. carbon.

The composition, size, amount of amorphous phases of four graphite and two coke materials were investigated to the purpose for correlating the structural features with the friction behavior. The morphological properties were evaluated by optical and electron microscopy (OM and SEM) while amorphous carbon content was evaluated by Raman spectroscopy. Both optical and electron micrographs allowed the calculation of the main morphological parameters, that were correlated to the friction properties, indicating as major result a direct proportionality between friction coefficient (COF) and aspect ratio [1]. Moreover, density significantly affects COF values: the friction coefficient decreases with the increase in density. A direct proportionality between particles size and COF is observed up to 250 μm size, while friction decreases for size below 250 μm.

All materials show common Raman spectral features in the 800 – 2000 cm^{-1} range, related to the so-called G and D peaks, which lie at around 1580 and 1350 cm^{-1}, respectively [2]. The effect of the amorphous carbon content is not yet clear, so further studies are needed to understand its influence on the friction behaviour.

As far as the influence of load and speed are concerned, the variation of COF shows a direct proportionality with the reciprocal of load for all carbon materials, while the sliding speed shows a limited effect.

A lot of study is still needed for a better understanding of the phenomena affecting friction properties. However, the authors believe that these first outcomes can represent a good starting point in terms of approach, that moves from trial and errors towards an aware and systematic method for the design of novel compositions for industrial applications.

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OR-12

Deoxydehydration of glycerol using rhenium-based catalysts

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[c] *Dipartimento in Scienze Filosofiche, Pedagogiche ed Economico-Quantitative, Università degli Studi"Gabriele D'Annunzio", Via dei Vestini 31, 66100-Chieti, Italia*
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Today new industrial processes starting from renewable feedstocks such as polyol derivatives are proposed to improve environmental conditions and to limit the use of non-renewable sources. Actually, there is a growing interest in catalytic deoxygenation methods, and especially in deoxydehydration (DODH). This reaction can remove two adjacent hydroxyl groups from vicinal diols to afford the corresponding unsaturated derivatives. The best performing catalysts for these reactions are rhenium-based [1,2].

Our group is expert in preparation, characterization and use of homogeneous catalysts to hydrogenation and deoxydehydration reactions [3]. In the present work, we describe a sustainable conversion of glycerol in allyl alcohol using several homogeneous catalysts from rhenium supported catalysts to Re^{III} and to Re^{V} compounds. Best results are obtained in presence of 1% commercial rhenium triphenylphosphine complexes (Figure 1).

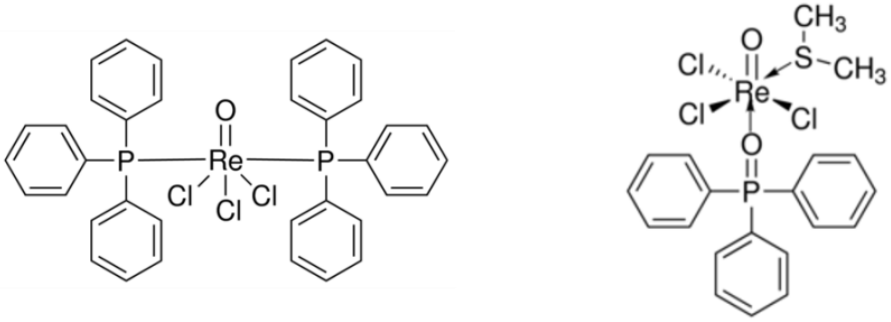

Figure 1: Two of rhenium based catalysts investigated.

[1] S. Raju, M. E. Moret and R. J. M. Klein Gebbink, *ACS Catal.* **5** (2015) 281-300.
[2] V. Canale, L. Tonucci, M. Bressan and N. D'Alessandro, *Catal. Sci. Technol.* **4** (2014) 3697-3704.
[3] K. Di Pietrantonio, F. Coccia, L. Tonucci, N. d'Alessandro and M. Bressan, *RSC Adv*. **5** (2015) 68493-68499.

OR-13

CO_2 and N_2O from wastewater treatment plants (WWTPs) determined by a new method based on gas-chromatography coupled to a barrier ionization discharge detector (GC-BID)

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Wastewater treatment plants (WWTPs) emit CO_2 and N_2O, which may lead to climate change and global warming effect. Over the last few years, there has been an increasing awareness of greenhouse gas (GHG) emissions from WWTPs [1,2]. Moreover, the development of valid, reliable, and high-throughput analytical methods for simultaneous gas analysis is an essential requirement in environmental applications. In the present study, an analytical method based on gas chromatography (GC) equipped with a barrier ionization discharge (BID) detector was developed for the first time. This new method simultaneously analyses CO_2 and N_2O and has a precision of 6.6% and 5.1%, respectively. Method-detection limits are 5.3 ppm_v for CO_2 and 62.0 ppb_v for N_2O. Selectivity, linearity, accuracy, repeatability, intermediate precision, limit of detection and limit of quantification provided good results at the trace concentration levels. After validation, the method has been applied to a real case of N_2O and CO_2 emissions from WWTPs, confirming its suitability as standard procedure for simultaneous GHGs analysis in environmental fields. The obtained results could contribute to the development of a standard methodology for gas sampling and measurement, not actually available. Moreover, monitoring of GHG emissions from WWTPs with our validated GC-BID method allows to improve the knowledge about biological processes and operational conditions in WWTPs and it is useful to develop new modelling approaches for lowering the environmental impact of water utilities and the Carbon FootPrint (CFP) of WWTPs [3].

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[3] D. Caniani, G. Esposito, R. Gori and G. Mannina, *Water* **7** (2015) 5599-5616.

OR-14

Biochemical and chromatographic approaches for oxytocin serum determination in former drug addicts

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Oxytocin (OXT, Figure 1) is a nonapeptidic hormone acting also as a neurotransmitter in human brain. OXT plays an essential role in a wide variety of physiological processes, including stimulating labor by uterine contraction, control of post-partum haemorrhage and lactation. Oxytocin is also involved in the modulation of a plethora of human behaviours influenced by environmental and social situations, from love and social bonding, to addiction vulnerability and relapse.

In order to investigate the complex relationships between OXT endogenous levels and conditions of vulnerability towards drugs of abuse, anti-social and dangerous behaviours, a multidisciplinary approach is required, having among its priorities the accurate, sound and reliable quantitative assessment of this pluripotent peptide in biological fluids.

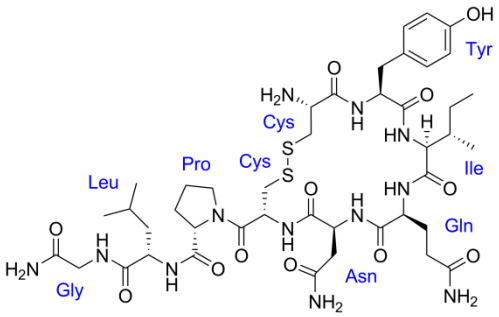

Figure 1: Chemical structure of OXT.

The objective of the present study was the development and application of a novel bioanalytical strategy to quantify endogenous OXT levels in serum samples coming from former drug addicts, recruited in collaboration with Italian addiction treatment structures.

Analytical methods for the determination of oxytocin need to be very sensitive and highly accurate, as circulating OXT serum levels likely to be low. For this reason, an optimised enzyme-linked immunosorbent assay (ELISA), coupled to spectrophotometric analysis, was used as a fast initial sample screening, whose quantitative results were confirmed by a LC-MS/MS method, thoroughly tuned in order to achieve the required sensitivity.

Method application to former heroin addicts and healthy volunteers, used as controls, is part of a wider interdisciplinary research project aimed at evaluating the role of oxytocin in drug addiction vulnerability and relapse, through a comparative study between serum levels and psychological and behavioural profiles deriving from psychometric tests.

OR-15

Mn_3O_4 nanofibers for oxygen reduction reaction catalysis

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Recently, the unique properties of transition metal oxides have attracted great attention as cathodic materials in the field of fuel cells. In this context the best electron acceptor is the oxygen molecule but, in order to exploit the Oxygen Reduction Reaction (ORR), a proper catalyst is needed [1], and platinum is considered the best one due to its high overpotential. Manganese Oxides (Mn_xO_y) are among the most promising substitutes combining good catalytic performances with environmental friendliness [1]. Several approaches have been proposed in the last years to nanostructure this catalyst to enhance its catalytic behavior. In this work we have optimized the Mn_3O_4 nanostructuration into nanofibers (NFs) by electrospinning, starting from a water-based solution of polyethylene oxide and manganese acetate [2]. Such NFs need a carefull thermal treatment in order to remove the polymeric templant and retain the NF shape. The morphological characterization and catalytic behavior of the resulting Mn_3O_4 NFs calcinated at 480°C are shown in Fig. 1, evidencing their nanostructure and an electron transfer number close to 3.7 below -0.4V. These results demonstrate that the Mn_3O_4 NFs represent a good and green alternative to Pt-based catalysts.

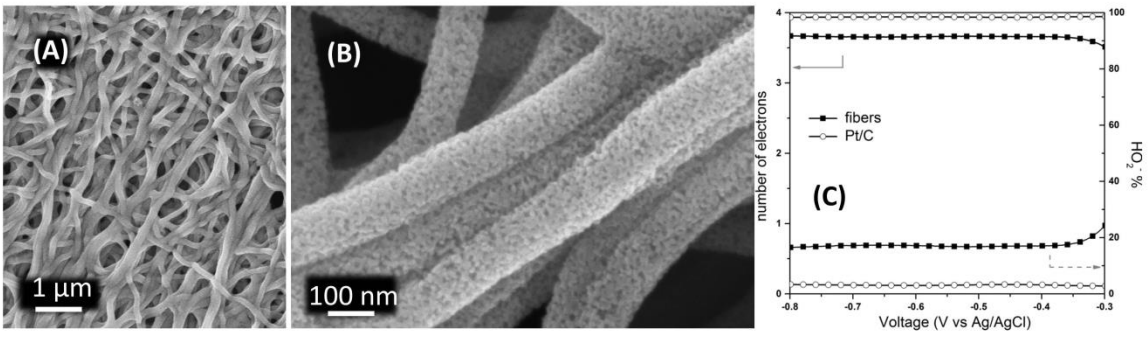

Figure 1: FESEM images of (A) the calcinated naofibers and (B) their enlargement. (D) ORR performance evaluated by RRDE.

This work have been financed by the ONRG, award number N62909-14- 1-N041.

[1] Z. Y. Zhou, N. Tian, J. T. Li, I. Broadwell and S. G. Sun, *Chem. Soc. Rev*. **40** (2011) 4167-4185.
[2] L. Delmondo, G. P. Salvador, J. A. Munoz-Tabares, A. Sacco, N. Garino, M. Castellino, M. Gerosa, G. Massaglia, A. Chiodoni and M. Quaglio, *Appl. Surf. Sci.*, DOI: 10.1016/j.apsusc.2016.03.224.

OR-16

2,3-dihydrobenzofuran neolignans: biomimetic synthesis and biological properties

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Lignans and the related neolignans are polyphenolic natural products widespread in plants and showing a variety of both structures and biological activities. These compounds are biosynthesized by radical oxidative coupling of two phenylpropanoid (C_6C_3) precursors. Among these, neolignans with a dihydrobenzofuran skeleton, originated through 8-5′ coupling, are reported for an array of biological properties including antioxidant, anti-inflammatory, antiviral, antitumor and antiangiogenic activities. Thus, we report here the biomimetic synthesis of new neolignans with a 2,3-dihydrobenzofuran core and a study of their biological properties.

Firstly we explored by molecular docking calculations the 2,3-dihydrobenzofuran scaffold to identify new lead compounds as potential inhibitors of microsomal prostaglandin E_2 synthase (mPGES-1). Compounds **1 - 4** were then synthetized from naturally occurring or bio-inspired caffeic acid esters, through an oxidative coupling reaction mediated by Ag_2O. These compounds were evaluated as mPGES-1 inhibitors.

Further work was dedicated to the eco-friendly, biomimetic synthesis of dihydrobenzofuran neolignans based on enzymatic oxidative coupling mediated by *Trametes versicolor* laccase. We obtained the racemic neolignanamides **5 - 13**, subsequently evaluated for antiproliferative activity on three tumor cell lines. The chiral resolution of some racemates was also carried out.

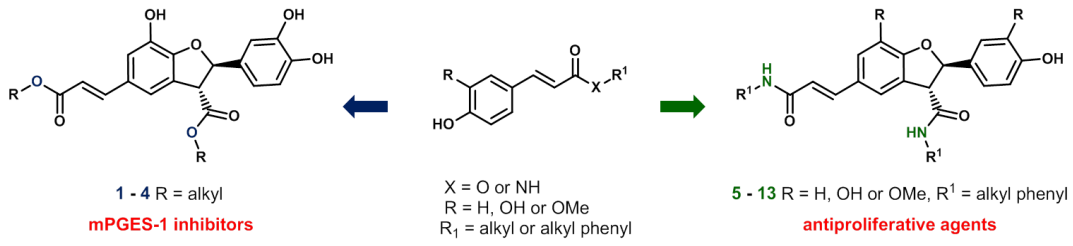

Figure 1: Schematic synthesis of dihydrobenzofurans **1** – **13**.

OR-17

Imaging meets lipidomics: an untargeted approach to skin lipids mapping

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Skin lipidomics (also referred to as *skinomics*) is the large-scale characterization of lipid profiles in skin and aims to elucidate possible mechanisms of diseases with a cutaneous pathological phenotype or the pharmacokinetic/pharmacodynamics profiles of topically administered drugs [1].

Matrix-assisted laser desorption/ionization (MALDI) imaging mass spectrometry (IMS) brings lipidomics studies to the spatial molecular characterization level [2].

A first attempt of the untargeted mapping of skin lipids by means of cheminformatics and data mining approaches will be presented, focusing on feasibility and warnings.

In particular, a workflow for efficiently maximizing the extraction of information from a typical MALDI-IMS analysis will be discussed and examples of preliminary results given.

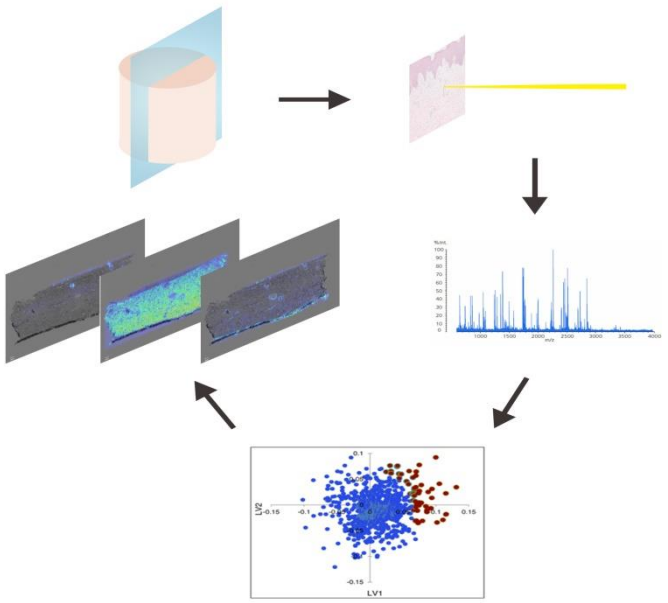

Figure 1: MALDI-IMS meets lipidomics: workflow schematization.

[1] S. Younis, M. Komine, M. Tomic-Canic and M. Blumenberg, *in Textbook of Aging Skin*, eds. A. M. Farage, W. K. Miller and I. H. Maibach, Springer Berlin Heidelberg (2014) 1-19.
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OR-18

Formaldehyde in emulsion polymers. A case history of how has been managed its gradual reduction / elimination

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Formaldehyde is widely used in many different industrial fields. Its main application is in the production of resins with urea, melamine and phenol, employed for manufacturing particleboard, plywood, and furniture. Formaldehyde is a key intermediate for the synthesis of many industrial chemicals; it's widely used also in the cosmetic industry, for textile applications and as disinfectant because of its broad spectrum of action on many microorganisms [1].

Nevertheless, considering its high toxicity, volatility and almost ubiquitous presence, formaldehyde has been recently included in the SVHC (substance of very high concern) list by the ECHA (European Chemicals Agency) as carcinogenic substance of category 1B [2]. As for other chemicals, the European and International legislations set restrictive limits for formaldehyde content and emission from the finished products, pushing toward a gradual reduction of this substance, or, if possible, a complete elimination.

VINAVIL S.p.a. (part of the Mapei Group) produces mainly vinyl- and acryl-based polymers latexes since almost a century and is the market leader in Italy. In this type of polymers formaldehyde is not a raw material, but can be present in traces as a by-product, depending on the specific technologies of production, or originating from particular species and additives used in formulation.

In this perspective, the approach followed by our research has been: where possible, the replacement of sources of formaldehyde with other equally effective or better performing chemicals (with particular regard on polymerization initiators, crosslinking monomers and bactericides systems); on the other hand, the use of particular molecules as *scavengers* of residual formaldehyde was developed, with the ultimate goal of achieving *'zero formaldehyde'* products.

Details of some chemical reactions which, in these products, release formaldehyde as a by-product will be illustrated, together with some examples of process technology modification and the use of selected additives for the reduction of residual traces.

[1] G. Reuss, W. Disteldorf, A.O. Gamer, and A. Hilt, "Formaldehyde", in "Ullmann's Encyclopedia of Industrial Chemistry", 6th edition.
[2] Classifications - CL Inventory, https://echa.europa.eu/it/information-on-chemicals/cl-inventory-database/-/discli/details/55163.

OR-19

Probing metal ion complexation of ligands with multiple metal binding sites: the case of spiropyrans

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Among molecular switches, spiropyrans attract considerable interest for their responsiveness to a variety of external stimuli and the deep physicochemical differences among the interconverting isomers, which make them particularly suitable for the synthesis of stimuli-responsive materials [1]. Metal coordination is one of the most interesting aspects of spiropyrans [2], however knowledge around the details surrounding spiropyran-metal ion binding is limited.

In this contribution we analyze the interplay between a spiropyran molecule specifically designed to display competing/collaborative metal binding sites, and Mg^{2+}, Cu^{2+} and Zn^{2+}, which usually display similar coordination geometry preferences while differing in their hard/soft character. Our results indicate that the three metal complexes obtained have similar coordination stoichiometry and morphology. Plus, the Mg^{2+} and Zn^{2+} complexes display fluorescence in solution and also visible light responsiveness [3]. These results provide important information that can serve as a foundation for rational design of novel functional materials for metal sensing and scavenging applications.

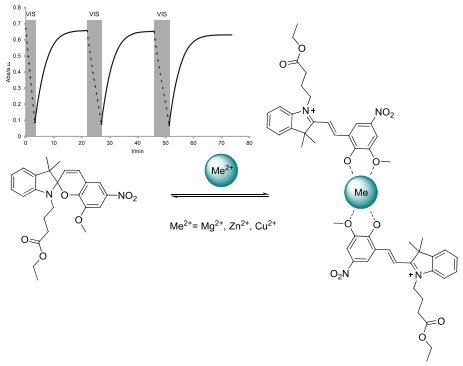

Figure 1: Reversible "catch and release" of metal ions from the spiropyran derivative.

[1] a) R. Klajn, *Chem. Soc. Rev.* **43** (2014) 148-184; b) M. Natali and S. Giordani, *Chem. Soc. Rev.* **41** (2012) 4010-4029.

[2] a) M. Natali, C. Aakeröy, J. Desper and S. Giordani, *Dalton Trans.* **39** (2010) 8269-8277; b) M. Natali and S. Giordani, *Org. Biomol. Chem.* **10** (2012) 1162-1171.

[3] M. Baldrighi, G. Locatelli, J. Desper, C. B. Aakeröy and S. Giordani, *Chem. Eur. J.* **22** (2016) 13976-13984.

OR-20

On the thermal and thermodynamic (in)stability of methylammonium lead halide perovskites

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The interest of the scientific community on methylammonium lead halide perovskites ($MAPbX_3$, X=Cl, Br, I) for hybrid organic-inorganic solar cells has grown exponentially since the first report in 2009. This fact is clearly justified by the very high efficiencies attainable (reaching 20% in lab scale devices) at a fraction of the cost of conventional photovoltaics. However, many problems must be solved before a market introduction of these devices can be envisaged. Conventional powder X-ray diffraction has been used to check the phase purity of the synthesized compounds. Later, we present and discuss the results we obtained using non-ambient X-ray diffraction, Knudsen effusion-mass spectrometry (KEMS) and Knudsen effusion mass loss (KEML) techniques on $MAPbCl_3$, $MAPbBr_3$ and $MAPbI_3$. The measurements demonstrate that all the materials decompose to the corresponding solid lead (II) halide and gaseous methylamine and hydrogen halide, and the decomposition is well detectable even at moderate temperatures (60 °C). Our results suggest that these materials may be problematic for long term operation of solar devices. The diffractograms of $MAPbCl_3$, $MAPbBr_3$ and show only the reflections of the desired compounds, with no lead halides detected.The compounds were then inserted into the non ambient chamber and underwent a thermal treatment under helium atmosphere from 130 °C to 170 °C with isotherms every 10 °C, each one lasting 10 hours. After each isotherm the sample was cooled to 25 °C and a diffraction pattern was taken. The temperature range was chosen in order to have detectable changes of the samples within the hours range of time. The phase identification analysis performed on the patterns revealed that the only solid decomposition product is the corresponding lead (II) halide for all the compounds under investigation. No trace of solid methylammonium halides has been found. This fact, together with the results coming from the Knudsen effusion-mass spectrometry (KE-MS) and Knudsen effusion mass loss experiments, demonstrate that the decomposition reactions occur in all cases with the loss of gaseous methylamine and the corresponding hydrogen halide according to the reaction:

$$MAPbX_3(s) \rightarrow PbX_2(s) + MA(g) + HX(g)$$

and not by phase separation of solid lead (II) halides and methylammonium halides, a possibility that had to be taken into account considering that all the methylammonium halides under consideration have melting points over 200 °C. After phase identification, the quantitative phase analysis was performed by applying the Rietveld method on the diffractograms. The order of reaction for the decomposition reactions has been determined by differential thermal analysis (DTA) of the compounds using the "shape index" of the endothermic decomposition peak in the thermograms. All the compounds decompose according to a first order kinetics. The estimated half-lives are 9, 12 and 170 days for $MAPbCl_3$, $MAPbBr_3$ and $MAPbI_3$, respectively.

[1] B. Brunetti, C. Cavallo, A. Ciccioli, G. Gigli and A. Latini, *Sci. Rep.* **6** (2016) 31896.

OR-21

Flow field-flow fractionation-based approach as analytical tool for nanomaterials design and risk assessment

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The access to suitable analytical tools for characterisation of nanoproducts is of primary importance, given their rising employment in technological and biological relevant applications. It is known that such materials undergo changes in composition, size, shape and core-shell properties during their life span. These modifications influence the overall activity and can cause adverse effects upon exposure [1].

Current characterization techniques like transmission electron microscopy (TEM) and dynamic light scattering (DLS) present various limitations: the introduction of an in-flow separation technique as a characterisation step provides reliable data regarding samples in suspension and collectable fractions to be individually characterised/tested [2,3]. In this presentation an analytical platform based on hollow-fiber flow field-flow fractionation (HF5) is presented, and its applicability onto different scenarios is detailed. The obtained results show its potential for the determination of the most relevant physicochemical properties of newly developed materials and related formulations both in healthcare and pharmaceutics.

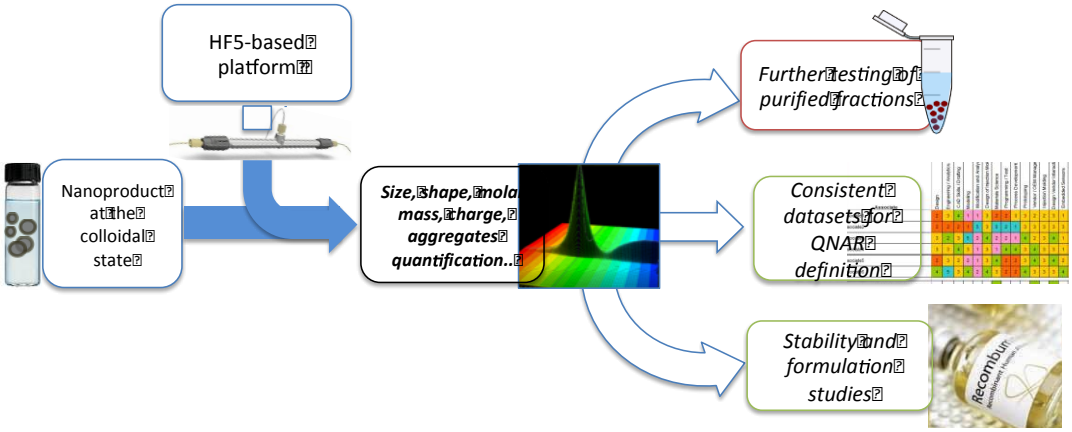

Figure 1: schematic view of the characterization workflow based on HF5

[1] E. Izak-Nau, A. Huk, B. Reidy, H. Uggerud, M. Vadset, S. Eiden, M. Voetz, M. Himly, A. Duschl, M. Dusinska and I. Lynch, *RSC Adv.* **5** (2015) 84172-84185.
[2] V. Marassi, S. Casolari, B. Roda, A. Zattoni, P. Reschiglian, S. Panzavolta, S. A. Tofail, S. Ortelli, C. Delpivo, M. Blosi and A. L. Costa, *JPBA* **106** (2015) 92-99.
[3] P. Reschiglian, B. Roda, A. Zattoni, M. Tanase, V. Marassi and S. Serani, *ABC* **406** (2014) 1619-1627.

OR-22

Smooth photocatalyzed benzylation of electrophilic olefins via decarboxylation of arylacetic acids

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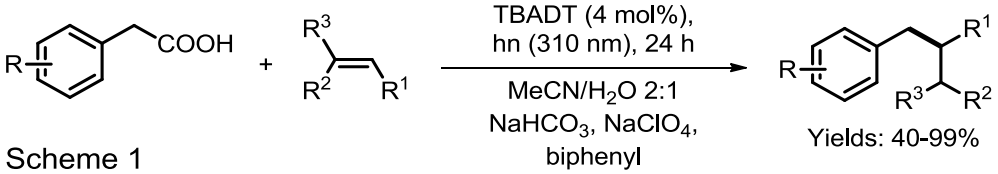
One of the major goals for organic chemists is to seek for ecosustainable synthetic approaches: among the others, two main factors should be considered, *viz.* availability and cost of the reagents and the possibility to adopt catalytic strategies.

In this regards, carboxylic acids are intriguing starting materials and recently have drawn great interest thanks to the role of the -COOH group as "traceless activating agent". This term is mainly due to the capability of this moiety to increase and direct the reactivity of an otherwise inert substrate, leaving no traces at the end of the reaction. One important application involves the use of acids in their anionic form (*i.e.* carboxylates) as precursors of radicals: in facts, after a monoelectronic oxidation, a molecule of CO_2 can be liberated yielding a carbon-centered radical [1]. A very efficient and ecosustainable way to run these reactions under mild conditions is to use a photocatalytic approach, where the excited catalyst is able to trigger the desired mono-electronic oxidation [2].

In this study, we focused our attention on α-arylacetic acids as precursors of benzyl radicals to achieve the photocatalyzed benzylation of electron-poor olefins. The reaction proceeds smoothly in the presence of catalytic amounts of a W-based catalyst, TBADT (tetrabutylammonium decatungstate, $(Bu_4N)_4[W_{10}O_{32}]$) under UV light (λ_{IRR} = 310 nm). The use of a base ($NaHCO_3$), a salt ($NaClO_4$) and a co-catalyst (biphenyl) is mandatory. The reaction tolerates several substituents on the aromatic ring (whether electron-donating or electron-withdrawing) and can be successfully extended to heteroaromatic analogues (see Scheme 1) [3].



Scheme 1

The present approach can be also extended to arylpropionic acids (including the nonsteroidal anti-inflammatory drugs ibuprofen and flurbiprofen), as well as mandelic acid derivatives [3].

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[3] L. Capaldo, L. Buzzetti, D. Merli, M. Fagnoni and D. Ravelli, *J. Org. Chem.* **86** (2016) 7102-7109.

OR-23

Total synthesis of the essential core of glycosylphosphatidylinositol for immunological studies on Paroxysmal Nocturnal Hemoglobinuria

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Glycosylphosphatidylinositols (GPIs) are glycolipids that are ubiquitously found in eukaryotic organisms where they are responsible for the anchoring of a variety of functionally diverse proteins to cell membranes [1].

All GPIs feature a common backbone consisting of three mannoses, one non-N-acetylated glucosamine and an inositol phospholipid, whose alkyl chains are inserted into the outer leaflet of the plasma membrane of cells; at the opposite far end of the molecule, the terminal mannose is connected to a residue of ethanolamine phosphate, which represents the anchoring point to the C-terminus of proteins.

Despite the pivotal role of GPIs in numerous biological functions, a full understanding of their structure–activity relationship is still elusive, largely because of the extremely limited quantities of GPI anchors available from natural sources and in high purity.

Chemical synthesis provides a valuable tool for tackling these issues, and it can supply both native and non-native GPI anchors [2]. In collaboration with Istituto Toscano Tumori, Giotto Biotech realized the total synthesis of the essential core of human GPI to be used for immunological studies on Paroxysmal Nocturnal Hemoglobinuria (PNH).

The devised synthetic strategy allows for further late stage chemical modification of the parent structure, thus enabling the access to a wide range of GPIs from different organisms. The synthesized molecule has allowed to understand that the disruption of GPI biosynthesis is the cause of one of the symptoms of PNH, Bone Marrow Failure (BMF). Indeed, it was demonstrated that BMF results from an autoimmune attack, whereby T cells target GPI in normal cells, whereas GPI-negative cells are spared, thus causing the progressive expansion of GPI deficient hematopoietic cells [3].

[1] M. A. J. Ferguson, T. Kinoshita and G. W Hart, "Essentials of Glycobiology", Chapter 11, 2009.
[2] B. Richichi, L. Luzzatto, R. Notaro, G. la Marca and C. Nativi, *Bioorg. Chem.* **39** (2011) 88-93.
[3] L. Gargiulo, M. Papaioannou, M. Sica, G. Talini, A. Chaidos, B. Richichi, A. V. Nikolaev, C. Nativi, M. Layton, J. de la Fuente, I. Roberts, L. Luzzatto, R. Notaro and A. Karadimitris, *Blood* **121** (2013) 2753-2761.

OR-24

Host-guest interaction as driving force for the synthesis of pillar[6]arenes with a close insight into the cyclization mechanism and the templating role of the guest molecules.

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In the past decade a new class of macrocyclic aromatic host molecules called pillar[n]arenes (**P[n]**) has been disclosed by Ogoshi based on the condensation reaction between para-bis-alkoxy benzene derivatives and paraformaldehyde [1]. The reaction is catalyzed by the presence of a Lewis or Brønsted acid, leading to the formation of macrocyclic structures containing five or six arene rings. A wide number of researchers focused on the improvements of their synthesis in order to have easy-to-access host molecules for applications in supramolecular chemistry. Increasing the selectivity in pillararenes synthesis represents still a crucial point in the development of new synthetic methods and therefore the templated approach shows great promises.

Following these leads we recently published a paper focused on the improved high yield syntheses of the larger **P[6]** bearing three different alkoxy substituents and templated by a series of small organic and organometallic cations such as tetramethylammonium chloride [2].

Under particular reaction conditions an higher selectivity between **P[6]/P[5]** has been reached and the mechanism behind this reaction has been further studied in the gas-phase by FTICR-MS. Further studies has been focused on the conversion mechanism of **P[5]** into **P[6]** [3].

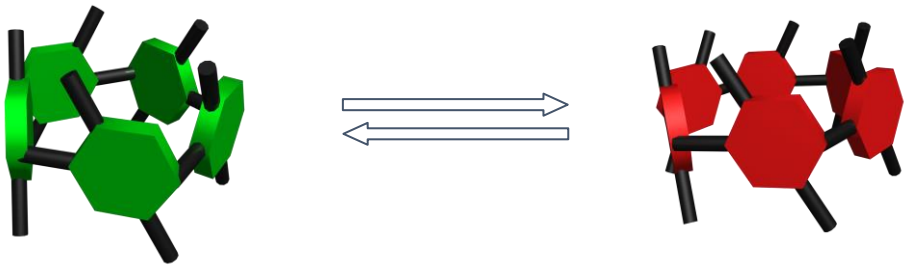

Figure 1: Conversion of **P[5]** into **P[6]**.

[1] T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.* **130** (2008) 5022-5023.
[2] M. Da Pian, O. De Lucchi, G. Strukul, F. Fabris and A. Scarso, *RSC Adv.* **6 (**2016) 48272-48275.
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OR-25

In situ generation of a family of substituted thioureas-cadmium thiocyanate coordination polymers: a crystal engineering study for new topologies and properties.

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Cadmium complexes can adopt different coordination typologies, depending on size, electrostatic and covalent bonding forces. Together with versatile ligands as thiocyanate ion is possible to develop an interesting chemical engineering of coordination polymers, because of its ability to act as a monodentate, bidentate or bridging ligand. Some coordination compounds of thiourea and cadmium have been reported [1] and they are of great interest for two main reasons: (i) the non-linear optical (NLO) properties of these compounds [2] and (ii) the convenient preparation of semiconducting materials through the thermal decomposition of these complexes [3]. We have prepared a series of organometallic polymers formed by a cadmium thiocyanate network and substituted thiourea with the aim to analyze the effects of the ligand anisotropy, hydrogen bond and halogens substitution in the ancillary ligands. We have synthetized and fully characterized five new coordination polymers of general formula $Cd(SCN)_2Rn$ (n=1 or 2) (R=thiourea, N-methylthiourea, N-phenylthiourea, N,N'-diphenylthiourea, N-1,3-difluorophenylthiourea). The synthesis of these compounds has been optimized by using an *in situ* generation of the cadmium thiocyanate, that induces the growth of big single crystals. These compounds show strong luminescence, and we tried a spectral interpretation by means of a computational analysis.

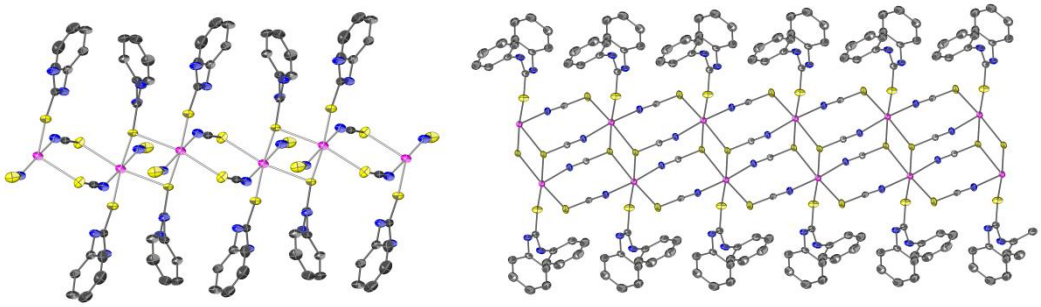

Figure 1: Polymer expansion of Cd(SCN)2$(phtu)_2$ (left) and $Cd(SCN)_2(ph_2tu)$ (right).

[1] A. Mietlarek-Kropidlowska and J. Chojnacki, *Acta Cryst.* **E68** (2012) m1051-m1052; X. Q. Wang, W. T. Yu, D. Xu, M. K. Lu and D. R. Yuan, *Acta Cryst.* **C58** (2002) m336-m337.
[2] V. Venkataramanan, C. K. Subramanian and H. L. Bhat, *J. Appl. Phys*., **77** (1995) 6049-6051; J. T. Yang, S. J. Luo, L. Yi and A. Laref, *Physica B* **408** (2013) 175-182.
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OR-26

Is there any future for p-type dye sensitized solar cells? How to improve the performance by lowering costs

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The future of p-type DSC, based on NiO, is nebulous. On one hand, this device could not be used as single junction photovoltaic cell because of their relative low overall efficiency (especially compared to n-DSC), on the other hand they could be couple with n-DSC in tandem cell in order to overcame the Shockley-Queisser limit.

Their employment as single junction device could became interesting by lowering costs production. In order to do that, the replacement of Pt counterelectrode with a cheaper material is mandatory [1].

The main goal to achieve in order to produce tandem device is the matching of the currents produced by the photocathode (p-side) with the photoanodic ones (n-side), that are quite higher. In NiO-based devices, the enhancement of the current density is thoroughly linked to the lowering of recombination phenomena. In order to do that two different routes could be undertaken: the realization of new NiO paste with a optimized morphology and the synthesis of dyes properly designed for application in p-type DSC.

These dyes should have a molecular structure that at the same time allows higher photon conversion and injection rate and minimizes the recombination phenomena [2].

Beside the pure photovoltaic employment as device able to convert the solar energy into electricity, the reductive property of p-DSC (contrary to n-type) could be very useful. Thanks to the coupling with proper co-catalyst NiO-based photocathode could be able to perform the sun-driven reduction of carbon dioxide as well as the solar production of hydrogen [3]. Nowadays the latter two employments are slightly more than an interesting awesomeness, but in a forthcoming future, they could determine the new life of p-DSC.

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OR-27

Fighting bacteria resistance: design and synthesis of new indole-based inhibitors for NorA efflux pump

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The antibiotic resistance is a worldwide threat causing serious concerns among scientific and medical community, especially regarding the outbreak of methicillin-resistant Staphylococcus aureus (MRSA). In particular, the overexpression of NorA efflux pump is the major self-defense mechanism developed from MRSA against common antibiotics. As result, the antibiotic is extruded trough the membrane causing the decrease of its concentration to sub-lethal level in the target.

Thus, drugging NorA pump is a valid option for recycling the by-now useless antibiotics, although remaining a challenging strategy, due to the little information available about this membrane protein. Being several indole-based compounds reported in literature as promising NorA inhibitors, we designed new derivatives which turned out to be active in low micromolar range [1]. Furthermore, an unattended dimer byproduct was also tested and, due to its surprising potency, further optimized through a *ligand-based virtual screening* approach [2], leading to the most active compound in our series.

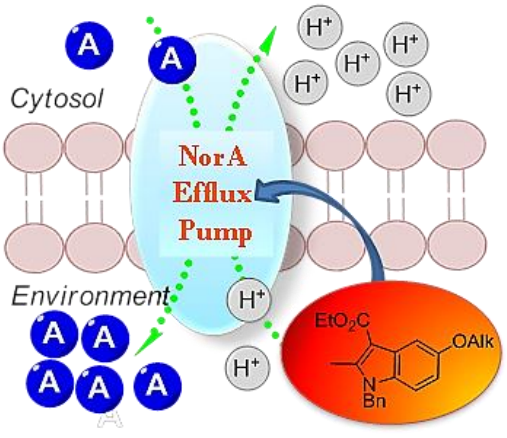

Figure 1: Indole-based compounds tested are able to inhibit antibiotic (A) extrusion through the bacterial membrane upon NorA efflux pump inhibition.

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OR-28
Controlled oxidation of MWCNTs at low temperature

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Carbon nanotubes (CNTs) are an allotropic form of carbon, extremely interesting for their electrical and mechanical properties [1]. Used as reinforcement in different matrices, CNTs present many problems due to their agglomeration and non-wetting surface, that can be solved by chemical functionalization [2]. In particular, when dispersion in common solvents or matrices is considered, it is necessary to have polar functional groups on the surface. Since oxygen-containing groups are easy to graft on the CNTs surface, oxidation seems to be the best way to guarantee improved surface polarity. Oxidation through acid attack has been extensively studied in literature [3], since this changes the CNTs hydrophilicity and improves their dispersion in various solvents. However, the use of acids creates numerous drawbacks such as a heavy damaging of the CNTs structure due to the aggressive environment present during the oxidation reaction.

This work originates from the need to find an oxidation method able to preserve the nanotubes structure while functionalizing the surface, in order to be able to disperse them in solvents or matrices but keeping the whole advantage given from the properties of the single CNTs. The idea was to perform a very simple oxidation of carbon nanotubes (CNTs) by thermal treatment at a specific temperature in controlled atmosphere. The conditions were chosen through a thermal gravimetric analysis (TGA) screening in a low oxygen (1-5%) atmosphere. The very initial phase of the thermal degradation starts between 350 °C and 450 °C, hence, the thermal degradation of CNTs was tested at lower temperatures with an isothermal treatment. By choosing the right temperature, time and amount of oxygen, it was possible to perform a precise and non-destructive oxidation of the CNTs, as demonstrated by several characterization techniques. This process enable the production of oxidized CNTs, which can be easily dispersed in aqueous solutions, without damaging the structure of the nanotubes.

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OR-29

Exploring cellular "comfort zone": cellular interactions with 2D organic monolayers

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Several works [1,2] report that cells behave differently if grown on a flat surface or on a nanometer-sized structure and how nanotopography impacts on cell morphology.
In order to study the effect of different chemical environments on cell structure and shape, disentangling the variations due to substrate morphology, we employed perfectly flat monolayers of different organic oligomers deposited by Organic Molecular Beam Epitaxy (OMBE) on SiO_x surfaces. The coverage of the substrates, that has to be as close as possible to 100%, was evaluated by Atomic Force Microscopy (AFM).

To investigate the adhesion of cells on the 2D organic monolayers, epithelial cells were cultivated on the samples and characterized by optical and fluorescence microscope as well as Scanning Electrochemical Microscopy.

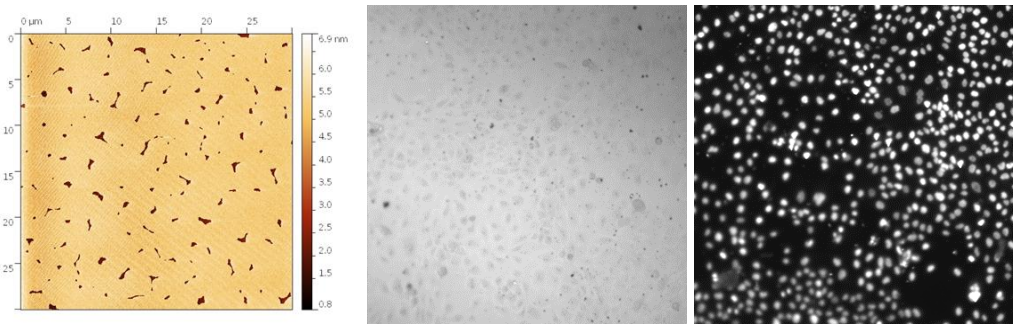

Figure 1: AFM image of a 6T monolayer, optical image and fluorescence of MCF10A cells grown on a 6T monolayer.

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OR-30

Supported gold nanoparticles for alcohols oxidation in continuous-flow heterogeneous systems

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Recently, we presented the preparation, without any need of additional reducing and/or stabilizing agents, of a variety of stable silica-supported gold nanoparticles (AuNPs) by using as the only reactants an aqueous solution of chloroauric acid ($HAuCl_4$) and different functionalized-silica supports. We started using commercial polyethyleneimine-functionalized silica bead [1] and we went on preparing silica nanoparticles with alkynyl carbamate moieties [2].

We now present the results of our recent work with supported AuNPs, which has been focused on the synthesis of a material with the right features for the application as catalyst in a continuous flow system. Indeed, flow chemistry is recognized by the Green Chemistry Institute (GCI) as a key area for research activities in the aim of developing sustainable manufacturing [3].

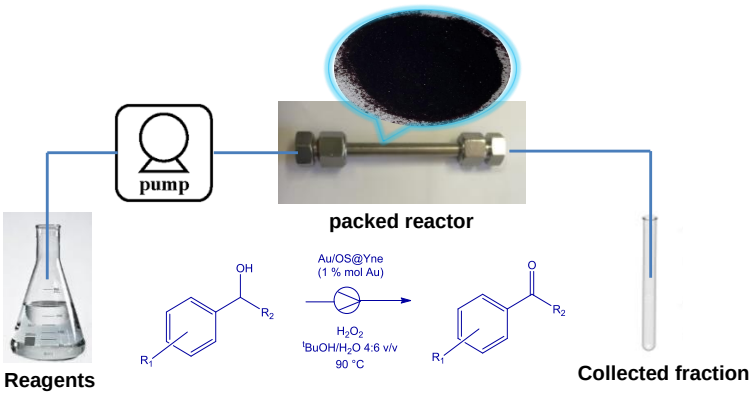

Figure 1: Continuous-Flow system employed for the alcohol oxidation.

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OR-31

Zn(II) multicationic porphyrazine complexes: photodynamic activity in aqueous media and *in vitro* tests

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Among the different areas of interest of the research group, extensive work has been done on the synthesis of porphyrazine macrocycles. Due to their strong electron-deficient nature, these systems have peculiar photochemical properties which make them excellent candidates as photosensitizers for the production of singlet oxygen ($^1O_2$), the main cytotoxic agent in Photodynamic Therapy (PDT). In particular, the Zn^{II} octacationic and Zn^{II}/Pt^{II} hexacationic macrocycles (salted by I^- ions; Figure 1A,B) showed a high activity in the photogeneration of $^1O_2$ both in organic solvent (DMF) [1] and in aqueous solution [2].

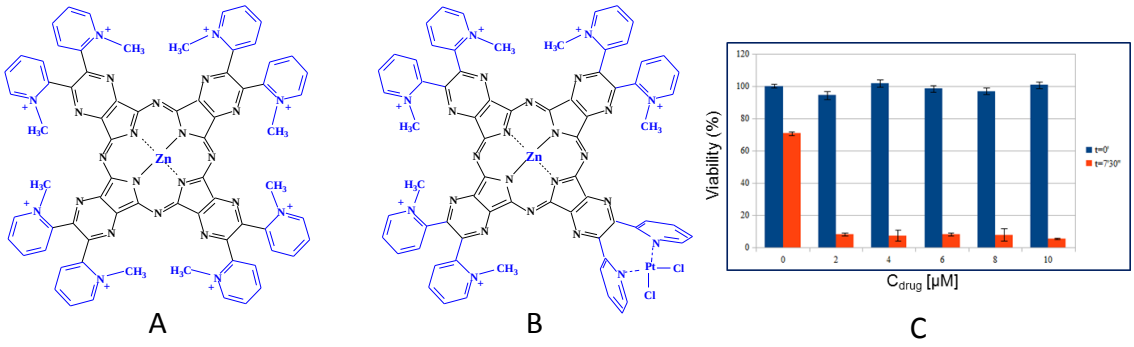

Figure 1: A) Zn^{II} octacationic macrocycle; B) Zn^{II}/Pt^{II} hexacationic macrocycle; C) cellular viability test for the Zn^{II} octacation at different concentrations of the photosensitizer, in the dark (t = 0') and after irradiation (t = 7'30'').

In order to test the therapeutic potential of the present compounds, *in vitro* tests were carried out on two different cell lines, the melanoma C8161 and the oral squamous carcinoma CA-1. The efficacy of the compounds was characterized in terms of cellular viability, cellular uptake, cell death modality and cell cycle distribution experiments [2]. Preliminary results on the cytotoxicity of the Zn^{II} octacationic complex are shown in Figure 1C.

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OR-32

Asymmetric transfer hydrogenation of imines mediated by phosphoric acids: from postulated to the experimental proof of reaction mechanism

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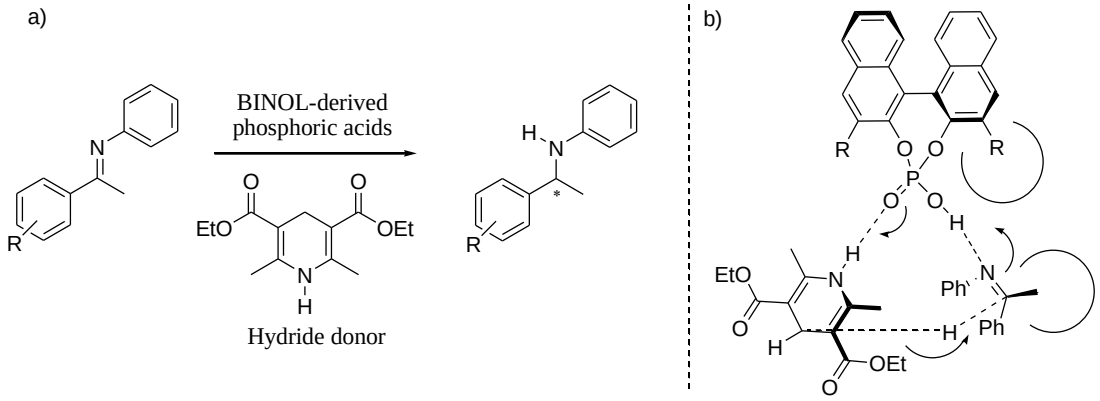
The organocatalytic asymmetric hydrogenation of ketoimines in the presence of Hantzsch esters as hydride source and BINOL-derived phosphoric acids as catalysts is a powerful transformation developped by the parallel work of List and Rueping groups in 2005 [1-2]. Analogous to Nature's NADH, Hantzsch esters have been shown to serve the role of small NADH analogues (Scheme 1a). Despite the importance of this reaction, which allows to synthesize chiral amine in a straightforward way, in high yield and high stereoselectivity, a compleate understanding of its mechanism is still lacking. Only proposed or calculated transition states are known in literature. In 2008, Goodman et al. proposed by DFT calculations a three points interactions model, in which a highly organised transition state is requested to reach high level of stereocontrol. From here, they postulated the existance of a ternary complex between the BINOL-derived catalyst, the imine and the Hantzsch ester (Scheme 1b) in which according to the stereoselectivity obtained the Z-imine should be the reacting specie [3].



Scheme 1: a) Organocatalytic hydrogenation of ketoimines; b) Postulated ternary complex by Goodman.

In this frame, I will present the first experimental proof of the postulated mechanism with a complete characterization by NMR of the reacting species for this transformation.

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OR-33

Amphiphilic peptides with controlled architecture for quantum dot functionalization towards biological applications

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Increasing attention is being devoted to quantum dots (QDs) as fluorescent probes to detect and image proteins and nucleic acids, as well as tracking drugs or biomolecules *in vitro* and *in vivo* [1,2]. Compared with organic dyes QDs possess several key advantages, which are essential for their application. For biological purposes, a carefully engineered surface functionalization of QDs is crucial to make them stable and biocompatible.

In this work, custom-designed amphiphilic peptides (APs), possessing hydrophilic backbones and functional groups, and hydrophobic acyl chains, have been synthesized as advanced and highly customizable encapsulation agents for protecting and functionalizing QDs. These peptides allow precision control of molecular architecture and precise positioning and density control of functional groups for further bioconjugation. Moreover, the rigid peptide backbone allows separation of hydrophobic/hydrophilic faces that can be modelled to optimize QD surface incorporation, stability, size and shape of final structures.

A comprehensive spectroscopic and morphological investigation of the functionalized QDs has been carried out to elucidate the role played by the different APs features in the functionalization procedure, in terms of size distribution and of the optical properties of the obtained systems. We have also performed conjugation of the prepared amphiphilic peptide capped quantum dots with DNA molecules to produce conjugate systems that are exceptional probes for a broad range of biomolecular detection and imaging applications.

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OR-34

Assisted assembly of a (μ_3-oxo)-tris(μ_2-peroxo)triiron(III) cluster in L-ferritins and its functional significance.

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Ferritins are ubiquitous multimeric protein systems showing a nanocage structure able to include thousands of iron atoms as oxoferric biomineral. In mammals, these twentyfour-mer protein shells are generally heteropolymers composed by two different types of subunits classified, according to their relative molecular weight, as heavy H and light L (183 and 175 amino acids, respectively, in human chains). The relative ratios between the two types in heteropolymers is tissue-dependent: ferritins in iron storage organs (e.g. liver and spleen) are richer in L-subunits, while those with fast iron metabolism (e.g. brain and heart) are richer in the H type. The H-subunit contains a ferroxidase center characterized by the so-called Fe1 and Fe2 sites and able to rapidly oxidize Fe^{2+} to Fe^{3+}. The ferroxidase process in ferritins was recently characterized by us through X-ray crystallography in a time-dependent iron loading study [1,2]. Accessories transient metal sites have also been identified in the proximity of the ferroxidase site and demonstrated to play a key role in the reaction turnover [1,2].

L-subunits lack the ferroxidase site, and hence iron incorporation in nanocages rich in L-chains is much slower. Nevertheless, homopolymeric L-ferritins are able to biomineralize iron. The proposed mechanism involves the presence of a putative nucleation site on the inner cage surface [3]. Through a time-dependent series of X-ray crystal structures of iron-loaded homopolymeric human L-ferritin we have observed the progressive formation of a triiron cluster on the inner cage surface of each subunit. After 60 minutes exposure, a fully formed (μ^3-oxo)tris[(μ^2-peroxo)(μ^2-glutamato-κO:$\kappa O'$)](glutamato-κO)(diaquo)triiron(III) anionic cluster was clearly visible in a structure determined at 1.98 Å resolution. A similar metallocluster was also observed in the lower resolution (2.22 Å) structure of horse spleen ferritin, suggesting that it represents a common feature of mammalian ferritins.

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OR-35

Proteomic and post-translational phosphorilations study of wild silk cocoon Cricula Trifenestrata and Bombyx Mori

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The development of functional materials that can interact with biological systems is nowadays of great interest. Such materials can be derived directly from nature or synthesized in the laboratory. However, despite the remarkable potential of man-made synthetics, their applications have been limited by challenges including biocompatibility, biodegradability and bioresorbability. The intrinsic advantages of natural materials lead to focus the research on silks, members of fibrous proteins family, with impressive mechanical strength, excellent biocompatibility, absence of immunogenicity, limited bacterial adhesion and controllable biodegradability.

Wild silks, not obtained from domesticated species, are primarily composed of proteins associated with certain macromolecules such as polysaccharides and lipids. The two primary proteins that comprise silk-cocoon silk are fibroin and sericin, consisting of 18 different amino acids: predominantly glycine, alanine and serine [1]. The amino acid sequences of silk proteins can vary from species to species, resulting in a wide range of mechanical properties [2].

This research is focused on wild silk cocoon of Bombyx Mori and Cricula Trifenestrata (no proteomic study has been done before on the latter) obtained from Indonesian source, and comprises a comparative proteomic analysis between the two cocoons and a final shotgun proteomic approach on the post translational modifications. In order to study these modifications, an upstream step of enrichment is required: for the specific enrichment of phosphopeptides, newly methods and stationary phases will be tested, i.e. coprecipitation methods [3] or spin columns with phosphate-specific-binding stationary phases.

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OR-36

Nanosized zinc salts as crosslinking promoters in model compound vulcanization

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Zinc oxide is extensively used in rubber chemistry due to its efficiency in activating the most important process in rubber industry: vulcanization. An adequate level of zinc oxide contributes markedly to chemical reinforcement, crosslink efficiency and many other rheological properties. However there is an increasing environmental concern about the release of zinc into the environment which may happen during tire production, disposal and also during service conditions. Specifically soluble zinc compounds have been classified as “dangerous for the environment” and “very toxic to aquatic organisms” by the European Union. In addition, zinc oxide is an expensive raw material and its price is expected to increase in the near future. Both environmental and economic reasons prompted the manufacturers to study how to reduce the amount of zinc oxide used in rubber.

An approach to address this challenge is based on the use of nanomaterials [1]. In this work we propose the synthesis and characterization of zinc phosphate and zinc silicate nanostructures to be used as novel activators for the sulphur vulcanization of rubber. The effect of these activators has been studied with the “Model Compound Vulcanization” approach, a useful technique to monitor the process on a laboratory scale [2]. An original HPLC elution method, following MCV, allowed the identification of the different species formed during the reaction with particular reference to crosslinked by-products. Zinc phosphate and zinc silicate based nanomaterials are able to activate the vulcanization process, displaying a crosslinking efficiency superior than zinc oxide especially when used at low amounts. A significant reduction of zinc content (-87%) can be achieved with little impact on crosslinks density and on the cure process when nanosized zinc phosphate is used.

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OR-37

From "common" copper complexes to "smart" redox mediators in DSSCs: the role of electrochemistry

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Production of electricity from the abundant and ubiquitous solar light could represent a real means to ensure a sustainable energy demands of humans, and dye-sensitized solar cells (DSSCs) can be one of the potential alternatives. In such a photoelectrochemical devices photon-to-electron conversion is possible exploiting a sensitized photoanode for light harvesting and a redox mediator for cycling of the device.

Electron mediators represent surely an intriguing challenge for synthetic chemists but, first of all, for electrochemists. In fact a perfect knowledge of their electrochemical features are among the most important prerogatives to identify promising candidates alternative to the benchmark I^-/I_3^- couple that it is far from being an ideal mediator.

In this context I will show how electrochemistry could make the difference [1], transforming "common" copper complexes in "smart" components acting as efficient electron shuttles in DSSCs able to neatly outperform iodine-based electrolyte [2,3], also reaching interesting conversion efficiency > 6% (Figure 1).

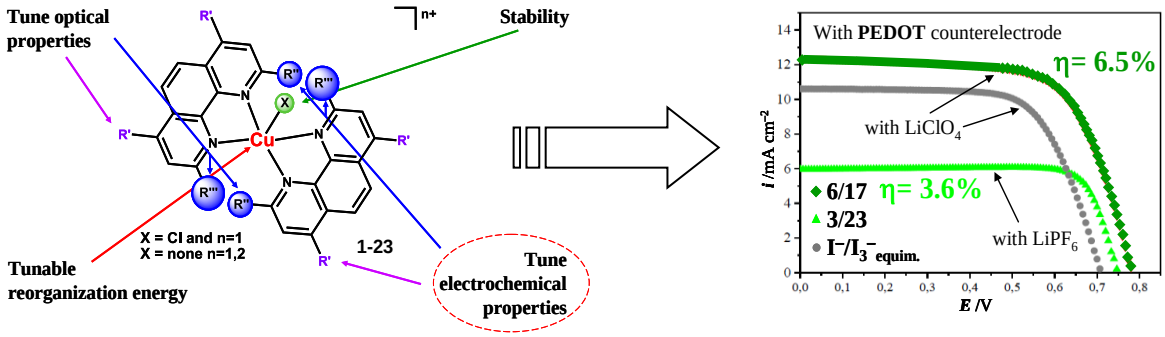

Figure 1: Graphic overview: from "fundamental" to "applicative" studies.

[1] M. Magni, A. Colombo, C. Dragonetti and P. Mussini, *Electrochim. Acta* **141** (2014) 324-330.
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OR-38

Development of enlarge pore size zirconium oxide nanoparticles and functionalization of nanoparticles for bio-medical applications

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Mesoporous nanoparticles (NP) with inorganic materials are attracting significant interest in many different areas of biomedicine due to their unique physical and chemical properties. Zirconia is chemically inert, biocompatible with good mechanical and thermal properties for in vivo biomedical applications [1]. Although the major limitations were the low surface area and small pore size, which are crucial for loading large biomolecules. Here, we report on the pore expansion of mesoporous zirconia by introducing different swelling agent together with hexadecylamine as neutral surfactant. SEM, TEM and N_2 adsorptions and desorption analysis demonstrate that not only mesopores were expanded to almost double the size (3.45 nm) of the original one (2.24 nm) but also spherical morphology and monodispersity were retained. In addition, Nanoparticles (NP) for biomedical applications must maintain colloidal stability under physiological conditions, NP carrying a payload such as drug molecules, metal complexes, antibiotics and proteins should be avoided premature release. So, chemical modification of the NP surface is essential for specific interactions with biomolecules of interest [2]. For this purpose, several bis-phosphonate (BP) compounds were prepared for functionalization of zirconia mesoporous nanoparticles. The compounds were characterized by different NMR spectroscopy and by GC-MS spectroscopy.

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OR-39

Development of new magnetic materials in shotgun phosphoproteomics

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Protein phosphorylation plays a critical role within cells, by regulating important pathways both in physiological and pathological conditions. However, the study of the phosphoproteome is still challenging, due to the low abundance of phosphoproteins and ion suppression phenomena during mass spectrometry. To bypass such issues, enrichment prior to analysis is fundamental [1], but currently no system is able to provide a comprehensive coverage of the phospohoproteome in complex systems [2].

In this context, the aim of our research was to develop new magnetic materials based on affinity chromatography for the selective enrichment of phosphopeptides. Magnetic solid phase extraction was preferred over other approaches due to its ease of use and versatility.

In one case, bare Fe_3O_4 magnetic nanoparticles were covered with polydopamine, which is a polymer easily produced by the spontaneous polymerization of dopamine under basic conditions, then exploited to immobilize Ti^{4+} cations on the surface of the nanoparticles. An optimized protocol was developed testing the material on a bovine serum albumin and casein (100:1) tryptic digest and commercial cow milk, with good results compared to a standard commercial enrichment kit.

In the second case, new composite magnetic phase was prepared exploiting affinity chromatography to TiO_2. Carbon materials, starting from graphitized carbon black (GCB), were employed to produce hybrid magnetic materials which coupled the large surface area of carbon materials with the selectivity for phosphopeptides by TiO_2 . This new phase was first tested on the standard mix and then optimized on a complex yeast extract. All enrichment methods were developed by a typical shotgun proteomics workflow, comprising nanoHPLC, high resolution mass spectrometry and bioinformatics data analysis, for full performance evaluation and comparison to established methods.

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OR-40

Fabrication and characterization of biodegradable elastomers based on cocoa shell waste with antioxidant capability

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Recently, food industry has shown great interest towards natural-based smart food packaging materials that can sense and delay food spoilage due to oxidation [1]. In chocolate industry around 0.5 million tons/year of cocoa bean shell are removed and discarded [2]. Cocoa shell waste is rich in lipids, lignin and polysaccharides as well as in polyphenols and other antioxidants [2,3]. It was reported that cocoa shell could effectively protect fatty foods against oxidative rancidity [2]. Hence, valorization of cocoa shell waste is of interest due to potential cost reductions and waste minimization in food industry.

In this study, we present a new strategy for the utilization of cocoa shell waste in the development of new biodegradable elastomers. The cocoa shell waste was first micronized and then incorporated into poly(dimethylsiloxane) (PDMS) macromolecular matrix by a simple mixing process to achieve bio-elastomers with tunable properties. It was found that the addition of cocoa particles had strong effect on the curing behavior of PDMS due to an intermolecular hydrogen bond network between the two components. Cocoa bio-elastomers were hydrophobic and exhibited good water barrier properties. In addition, the biofilms showed efficient antioxidant scavenging activity against 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH$^{\bullet}$). The incorporation of micronized cocoa waste into PDMS was also found to significantly enhance the biodegradability and the Young's modulus. Therefore, these bio-elastomers can potentially be used as active and intelligent food packaging materials.

Figure 1: The fabrication of cocoa bio-elastomer from cocoa shell waste.

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[3] B. Sarriá, S. Martínez-López, J. L. Sierra-Cinos, L. Garcia-Diz, L. Goya, R. Mateosand and L. Bravo, *Food Chem.* **174** (2015) 214-218.

OR-41

Innovative photoreactors for unconventional sustainable processes

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The development of new photoreactor configurations is a fundamental research topic for the transition from the lab-scale to the industrial application. Two main challenging processes were studied: i) Photo-abatement of N-containing pollutants from waste water; ii) CO_2 photoreduction to chemicals and fuels.

In this research, we show case studies of novel concepts of photoreactor developed by our group [1]. In addition several nanostructured photocatalysts were prepared and tested for the abatement of N-containing compounds, focusing on selectivity towards innocuous N_2. Part of the photocatalysts have been prepared in nanosized form by using an innovative flame pyrolysis (FP) approach, able to synthesise in one step single or mixed oxide nanoparticles, characterized by homogeneous particle size and good phase purity. Doping of the sample with Au (0.1-0.5 wt%) [2] was investigated. The FP procedure proved an interesting method for the preparation of nanostructured Ti-based photocatalysts.

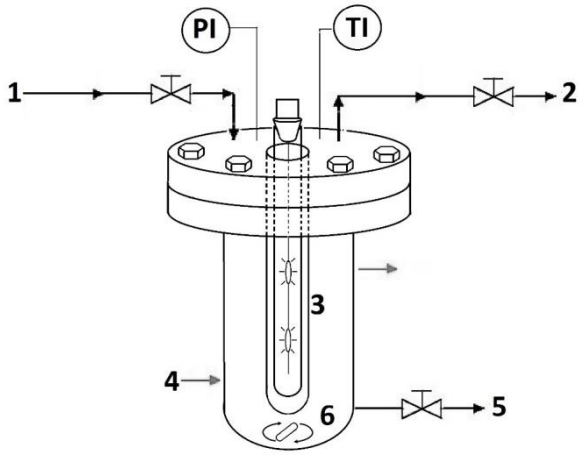

Figure 1: Sketch of the high pressure photoreactor.

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OR-42

Imidazolium-branched polysiloxanes as effective gel electrolytes for highly stable dye solar cells

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Among various alternatives to liquid electrolytes for dye sensitized solar cells (DSSC), polymer gel electrolytes (PGEs) still provide the greatest potentialities in the perspective of a successful commercialization of this technology, as they properly fill the gap between high performance and long term stability [1]. Because of the high flexibility of Si-O bond, high free volume, good thermal and chemical stability, polysiloxanes offer all the necessary prerogatives to play an important role in this field. We here report the implementation of poly[(3 methylimidazoliumpropyl) methylsiloxane-codimethylsiloxane] iodides (IP-PDMS) as suitable polymeric hosts for two novel class of linear and *in-situ* cross-linkable iodine/iodide-based PGEs for DSSCs [2]. We thus implemented it in a series of quasi solid-state DSSCs, which were monitored for 1000 h in accelerated aging conditions and they were found to maintain 90% of their initial energy conversion efficiency.

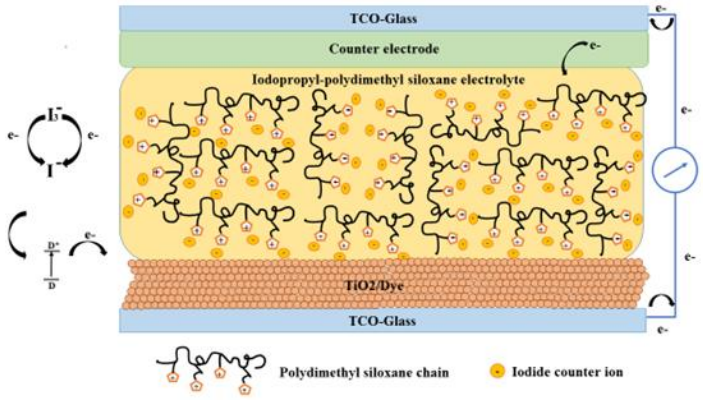

Figure 1:Schematic overview of the investigated devices

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OR-43

Synthesis of poly(carbazole)s: tailoring optical properties through polymer stereoregularity

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Carbazole-based compounds are attractive above all as photoconductors or charge-transporting materials. Among carbazole-containing polymers, poly(N-vinylcarbazole) (PVK) was the first to be synthesized and, despite its low electrical conductivity, has been used in combination with other layers in the fabrication of organic light emitting diodes (OLEDs). From the structural point of view, carbazole containing polymers can be divided into two groups: polymers with in-chain isolated carbazole groups and polymers with pendant carbazole groups, like PVK . In particular, it was found that, for the latter class of polymers, photoconductivity is affected by the stereochemical configuration of the polymer chain and the chemical nature of the spacer linking the chromophores and the main chain [1-3].

In this contribution, the synthesis of stereoregular poly(carbazole)s presenting different spacers linking pendant carbazole groups to the main chain by using homogeneous Ziegler-Natta catalytic systems is presented.

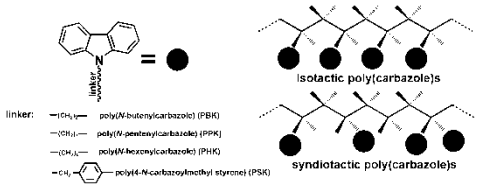

Figure 1: Structures of synthesized polymers.

Achieved polymers have been fully characterized by NMR, FT-IR, X-ray diffraction and thermal analysis and UV-Vis as well as photoluminescence have been also carried out. Therefore, a comparison between the chemico-physical properties and the optical behaviour of polymers is reported. The optical analysis of all polymer film samples reveals the presence of two different excimers arising from a fully ("sandwich-like", low energy excimer) or partially overlapping (higher energy excimer) of two carbazole group. Nevertheless, in isotactic polymers the emission intensity ratio between "sandwich-like" and "partially overlapping" excimers is higher than in syndiotactic. Thin films of achieved polymers have been tested as single emissive layers of OLEDs. A blue light is obtained from all the devices, except for the isotactic poly(*N*-pentenylcarbazole)-based OLED with an optimized architecture that emits a white light. From this comparison, the influence of the stereoregularity of polymer chains on the optical properties of poly(carbazole)s has been also investigated.

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OR-44

EEM fluorescence to the characterization and monitoring of humic-like substances (HLS) used as an additive in photo-Fenton process

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Fluorescence excitation-emission matrix (EEM) spectroscopy has been demonstrated as a sensitive technique to analysed dissolved organic matter (DOM), since its concentration and chemical composition influences the intensity and shape of the fluorescence spectra [1]. Parallel factor analysis (PARAFAC) has probed its ability to reliably decompose EEMs into independently varying fluorescent components [2]. On the other hand, Humic-like substances (HLS) obtained from urban wasted are able to expand the pH region of the photo-Fenton processes until near neutral pHs [3]. To this end, the interaction between HLS and Fe(III) and different photochemical experiments (in the absence and presence of H_2O_2) were studied at three different pHs. PARAFAC was used to characterize the EEM dataset from HLS, HLS-Fe and HLS during the photochemical degradation at three different pH. Three components were identified for the all cases in the three pH studied. The complexation constant value calculated using Ryan and Webel model was high at pH 5.

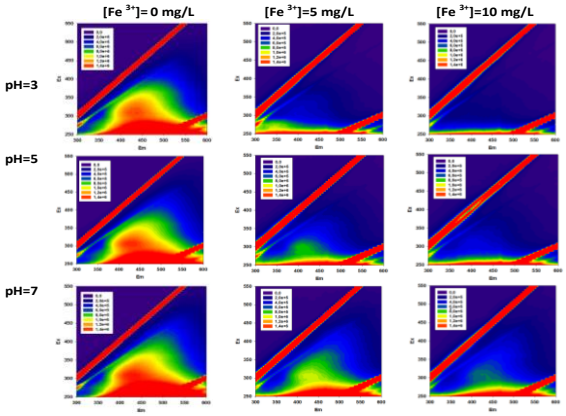

Figure 1: HLS fluorescence intensity changes with increasing iron concentration for pH 3, 5 and 7.

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OR-45

New mannosylcalixarenes as ligands for the inhibition of HIV/DC-SIGN interaction

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The fight against human immunodeficiency virus is a big challenge of current times and huge efforts have been made to develop new effective therapies [1]. One of the main pathway of infection exploits dendritic cells (DCs) that, used by the virus as Trojan horse, efficiently transfer virions to T-cells, where replication takes place [2]. Among receptors on DCs surface, DC-specific ICAM-3 grabbing non-integrin (DC-SIGN) is strongly involved in the process, by interacting with the high-mannose glycans of glycoprotein gp120 present on the virus envelope. Therefore, different research groups are focusing their work on the development of glycomimetic compounds that could interfere with gp120/DC-SIGN interaction and a multivalent approach seems to be a valuable strategy to improve ligands efficiency and selectivity. In this context, we designed and synthesized a small series of mannosylated calixarenes (Figure 1). The possibility of tuning valency and geometry of the ligating units makes calixarenes very convenient scaffold for multivalent ligands [3]. Preliminary experiments by Surface Plasmon Resonance evidenced the ability of our compounds to bind to DC-SIGN.

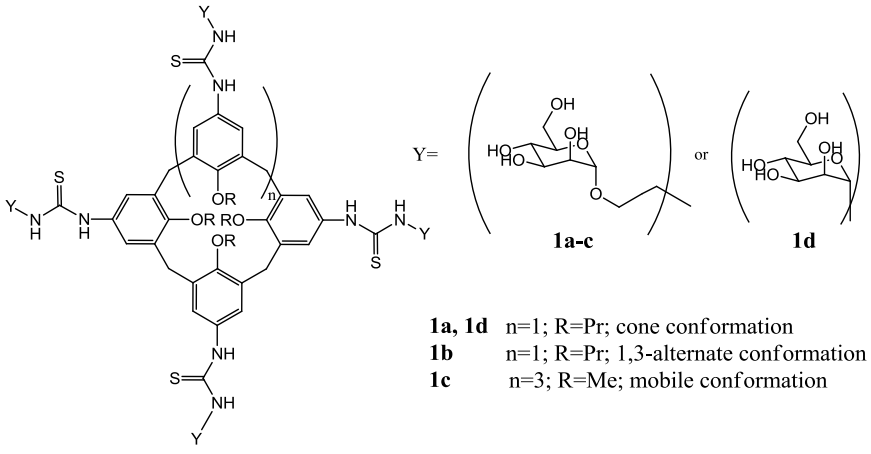

Figure 1: Mannosylated calixarenes.

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OR-46

Lipid-based nano-sized vesicles for the treatment of airway diseases

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Pulmonary drug delivery is the first choice for the treatment of airway diseases. In pathological conditions, such as asthma, bronchitis, cystic fibrosis (CF) and chronic obstructive pulmonary disease (COPD), a highly viscoelastic mucus hypersecretion occurs finally causing airway obstruction. For pulmonary administration a promising approach seems to be the use of nano-sized drug delivery systems, such as lipid-based nanocarriers, due to their good biocompatibility and biodegradability, formulation stability, reduced side effects and sustained drug release [1]. In this way, the aim of this work was the development of lipid-based nanosystems for the pulmonary delivery of Beclomethasone Dipropionate (BDP), selected as an anti-inflammatory model drug. In addition, these vesicles were surfaced-modified with amphiphilic polymers, such as PEG-lipids and PLURONIC F127, to test if they were able to improve the vesicles' steric stabilization and their mucus penetrability. A suitable modification of the "Micelle-to-Vesicle Transition" (MVT) method was tailored to prepare small unilamellar vesicles (≈100 nm) including BDP. The liposomal formulation was optimized in terms of size and drug encapsulation efficiency. The nanovesicles' toxicity was evaluated on NCI-H441 (human lung adenocarcinoma epithelial) cell line by MTT cytotoxicity assay highlighting that these systems were no cytotoxic. In addition, bronchoalveolar lavage was carried out in Swiss mice, confirming that the vesicles were no toxic in vivo too. The internalization into cells was evaluated by cytofluorimetry. Bioluminescence studies demonstrated a local more than systemic drug delivery. Finally, mucus-penetration studies were carried out on the mucus of COPD afflicted patients, which were enrolled at the Respiratory Clinic of Ospedali Riuniti of Foggia (Italy). This study highlighted that the designed SUVs were very promising in the treatment of airway diseases.

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OR-47

Untargeted profiling of a strawberry extract by ultra high performance chromatography coupled to high resolution mass spectrometry

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Untargeted metabolite profiling is a major challenge in metabolomics because of the huge chemical diversity of unknown substances. High resolution mass spectrometry, able to provide accurate mass of unknown compounds, is usually interfaced with a separation technique necessary to efficiently separate isomeric metabolites otherwise indistinguishable [1]. Optimizing the chromatographic and mass spectrometric conditions in an untargeted analysis could be crucial for the detection of the major number of compounds. Only few works on chromatographic method optimization and on the investigation of the optimal data acquisition for routine applications by means of Orbitrap mass spectrometers have been published till now. For this reason, we decided to explore the potentiality of the coupling of one of the most performing UHPLC system on the market with a Q Exactive mass spectrometer, which capabilities in metabolomics analysis have not been fully investigated yet.

In this work, we present a chromatographic and mass-spectrometric method optimization to obtain a complete profiling of a strawberry extract. Briefly, strawberries were extracted and analyzed with seven chromatographic different methods and with six different mass-spectrometric methods. Each method was evaluated by processing accurate mass ion chromatograms with the open source software MZmine v2.19 [2]. The method with the largest number of both MS features and MS/MS mass spectra was chosen to analyze the strawberry extract for identification. The main classes of polyphenols studied were flavonoids, phenolic acids, dihydrochalcones, ellagitannins and proanthocyanidins.

The optimized method allowed to identify 131 compounds, 74 of which have never been found in strawberries, and 22 of which have never been reported, to the best of our knowledge. The results clearly show the importance of a deep investigation on chromatographic and mass-spectrometric conditions prior to the untargeted profiling of complex phytochemical mixtures, suggesting to use this meticulous approach in all untargeted metabolomics analysis.

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OR-48

An unprecedented synthesis of dibenzo[1,5]diazocyne ring from α-β-ynones

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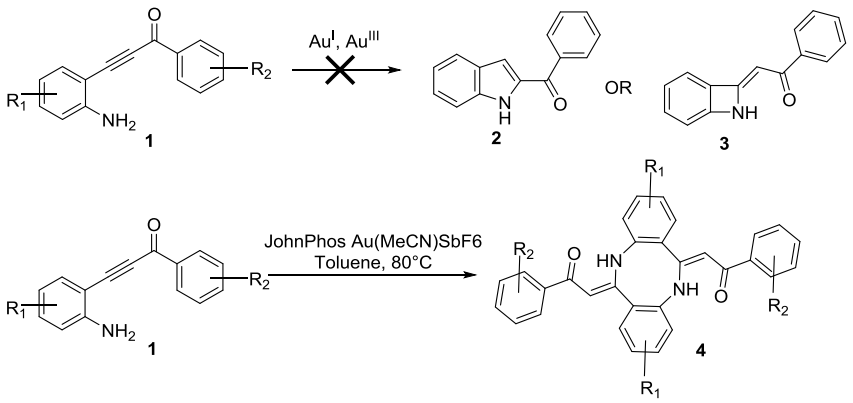
Dibenzo[1,5]diazocyne have found applications in supramolecular chemistry such as fluorescence probes for the imaging of cell compartments [1] and as chemosensitizers [2] in medicinal chemistry.

We wish to report here that, in the presence of suitable cationic Au(I) catalysts, β-(2-aminophenyl)-α,β-ynones **1** undergo an unprecedented reaction, affording interesting 8-membered benzodiazocyne ring **4**.

Using the reaction conditions previously developed by us for the cyclization of 2-alkynylanilines to indoles (Au^{III}, r.t.) we failed to observe any cyclized product starting from substrates **1** [3]. Increasing the temperature resulted in low conversion, with formation of a small amount of **4**. We then switched to cationic Au^{I} catalysts, and we observed a more efficient formation of **4**: the use of $ClAuPPh_3$/AgOTf resulted in a cleaner reaction mixture, with low byproducts formation. However **4** was still detected in unsatisfactory yield. Preformed cationic complex with triflimide counterion afforded better results and finally we observed that commercially available **JohnPhos Au(MeCN)SbF_6** lead to quantitative conversion of **1** and good yield of products **4**. Products **2** and **3**, deriving from *5-endo* or *4-exo* cyclization modes, were not isolated.



Scheme 1: Gold catalysed cyclisation of α,β-ynones.

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OR-49

Dye-sensitized solar cells based on eco-friendly nature-inspired deep eutectic solvent-water electrolyte solutions

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Among the new approaches to solar energy conversion, dye-sensitized solar cells (DSSCs) hold promise for high conversion efficiencies and low-cost manufacturing. Record efficiencies of 15% have been recently achieved. Unfortunately, one of the major drawbacks in these record cells is the presence of toxic volatile organic solvents in the electrolyte with an heavy impact on the environment.

Some efforts have been made in using water as the electrolyte solvent, but DSSCs proved to be typically unstable in this solvent. Thus, we have turned our attention towards non-hazardous, unconventional reaction media such as deep eutectic solvents (DESs). DESs are the combinations of two or three safe and inexpensive components which are able to engage in hydrogen-bond interactions with each other to form an eutectic mixture with a melting point much lower than either of the individual components [1]. Compared to traditional ionic liquids based on imidazolium salts which share low volatility with, DESs are simpler and cheaper to synthesize and do not need purification. In addition, DESs show high electrochemical conductivity and are biodegradable. One of the most common DES components, choline chloride, is produced on the scale of million metric tons per year as an additive for chicken feed. DESs are thus attracting increasing interest in both academia and industry [1].

In this study, we report our preliminary results on DSSCs containing DES-water mixtures as the electrolytes, with water content up to 40%, sensitized by multi-branched phenothiazine dyes developed in our group [2,3]. Not only are DES-water-based DSSCs eco-friendly, but also exhibit sufficient stability for long-term outdoor applications due to their low volatility. In particular, we have systematically varied the amount of I_2 and I^- in the absence or presence of imidazolium salts and co-additives, so as to improve current and photovoltage. Though efficiencies are still modest, this unprecedented class of electrolytes is promising for low-cost and environmentally safe applications of solar cells.

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OR-50

New core-shell and sub-2µm fully porous particles used as stationary phases for ultrafast high-performance enantioseparations

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In the last decade, column manufacturers have put much effort into the design and packing of materials (in particular, sub-2µm fully porous and core-shell particles) suitable for highly efficient and fast separations in ultra-high-performance liquid chromatography (UHPLC) [1]. As a matter of fact, however, this advancement has only partially interested the field of chiral liquid chromatography. This is essentially due, on the one hand, to the lack of interpretation of complex mass transfer processes in chiral chromatography and, on the other, to the difficulty in the functionalization of small particles with chiral selectors.

In this work, a new type of chiral stationary phase (CSP) for enantioselective ultra-high performance liquid chromatography (e-UHPLC) is presented. A brush-type chiral selector (Whelk-O1) was used to functionalize both core-shell and fully porous silica particles of different diameter (including also sub-2µm fully porous ones). The CSPs were slurry packed at high pressure into columns of different geometries. The kinetic performance of these columns was evaluated in normal phase conditions for the separation of the two *trans*-stilbene oxide (TSO) enantiomers.

To further assess the potential of these new CSPs in ultrafast enantio-UHPLC separations, a 10×3.0 mm (length × internal diameter) column packed with Whelk-O1 sub-2µm fully porous particles was operated at a very high flow rate (8 mL/min) to perform the separation of TSO enantiomers in less than one second [2].

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OR-51

Synthesis of trifluromethyl 2-imidazolines through Mannich-type reactions of isocyano acetates

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Fluorine is a special element, thanks to its electronic properties and its small size it can make drastic and often unexpected changes in physical and chemical properties, reactivity and biological characteristics of organic molecules [1]. However, fluorine-containing compounds rarely occur in nature but an increasing number of synthetic bioactive pharmaceuticals and agrochemicals contain fluorine. In many such compounds, fluorine is incorporated in the form of a trifluoromethyl group, which is well accepted in medicinal chemistry as a substituent of typical qualities.

Given the importance of trifluoromethyl groups in bioactive compounds and the fact that a large majority of modern medicines and agrochemicals contain one or more heterocyclic rings, the nitrogenated trifluoromethyl heterocycles are becoming modern attractive targets in the medicinal chemistry. In this field, 2-imidazolines have emerged as attractive synthetic targets due to their wide applications in the natural product chemistry, in coordination chemistry, and even in homogeneous catalysis [2].

We report here the first successful attempt to obtain trifluoromethyl 2-imidazolines through Mannich-type/cyclization cascade reaction of substituted α-isocyano acetates to trifluoromethyl aldimines [3].

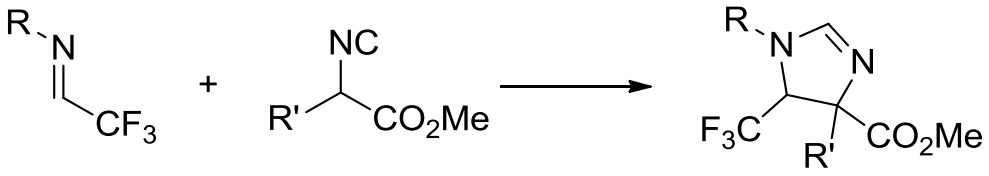

Figure 1: Synthesis of trifluoromethyl 2-imidazolines.

The stereoselectivity of the reactions can be successfully controlled when R is an L-α-amino ester residue, thus obtaining enantiopure valuable trifluoromethyl imidazolines enriched by an α-amino acid residue.

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OR-52

Gas-phase propionic acid synthesis from propylene glycol

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Here we report about a new route for propionic acid synthesis starting from propylene glycol (PG). Within the concept of oil-based biorefinery, this process would provide the opportunity to produce propionic acid from biomass resources. Indeed, PG can be readily produced from bio-glycerol by means of hydrogenolysis, and this process has already been commercialized on an industrial scale since 2010.

The overall transformation from PG to propionic acid includes two reaction steps: i) PG dehydration to propanal, promoted by acid catalysis, and ii) propanal oxidation to the corresponding acid, that needs redox catalysis. First, the two steps of the process were separately investigated: PG dehydration was performed over two different phosphate catalysts (a commercial V-P-O [1] and an AlPO catalyst), whereas propanal oxidation to propionic acid was carried out over a Mo-V-W mixed oxide.

Since propanal is industrially mainly employed as a chemical intermediate, and propionic acid is one of the main compounds produced from propanal, the one-pot gas-phase transformation of PG into propionic acid would represent the ideal option from the process configuration point of view. Hence, PG conversion was further investigated over different multifunctional acid and redox catalysts that were previously proved to be effective for the analogous one-pot transformation of glycerol into acrylic acid: a commercial V-P-O catalyst [1] and W-(Mo)-V-O mixed oxides with hexagonal tungsten bronze (HTB) structure [2]. Interestingly, despite the major similarities between the molecules involved in the two processes, when feeding PG on these multifunctional catalysts, very low yields into propionic acid were observed. Therefore, an in-depth investigation was performed with the aim to understand how the different reaction parameters and catalysts physicochemical features affect PG conversion on multifunctional materials. This study allowed us to shed light on the complex reaction network and understand which are the main critical points of the PG-to-propionic acid one-pot process, finally suggesting several key features to follow for the development of new catalysts.

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OR-53

pH and thermo-sensitive self-assembling properties in aqueous solution of the lipopeptide lauryl-Gly-Gly-D-Ser-D-Lys-NH_2

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Lipopeptides are hybrid biomaterials obtained by conjugating fatty acids and hydrophilic peptides that are able to self-assemble in nanostructures useful for drug delivery, imaging, and applications in gene therapies. Lipopeptide self-assembly depends on the hydrophile/lipophile balance of the molecules and on the peptide portion that are able to adopt predesigned secondary structure and respond to external stimuli such as pH and temperature [1]. Herein, the self-assembling properties of the lipopeptide lauryl-Gly-Gly-D-Ser-D-Lys-NH_2 are investigated. The amphiphilic lipopeptide was synthetized by solid-phase synthesis and characterized by circular dichroism (CD) and fluorescence spectroscopies, dynamic light scattering (DLS), rheology, and TEM microscopy. The sensitivity of the lipopeptide self-assembly was investigated at various temperatures and pHs exploiting the presence of the amino group in the side chain of the lysine residue. Preliminary results obtained by CD spectroscopy, DLS, and TEM microscopy showed that at acidic pH the peptide region is mainly in random coil and the lipopeptide self-assemble in spherical micelles (Figure 1A). By increasing the pH, the secondary structure of the peptide undergoes a cooperative transition from random coil to β-sheet forming a gel in about 12 hours. Rheological measurement clearly indicated the formation of solid-like gel where the lipopeptide is organized in nanofibres as supported by TEM images (Figure 1B).

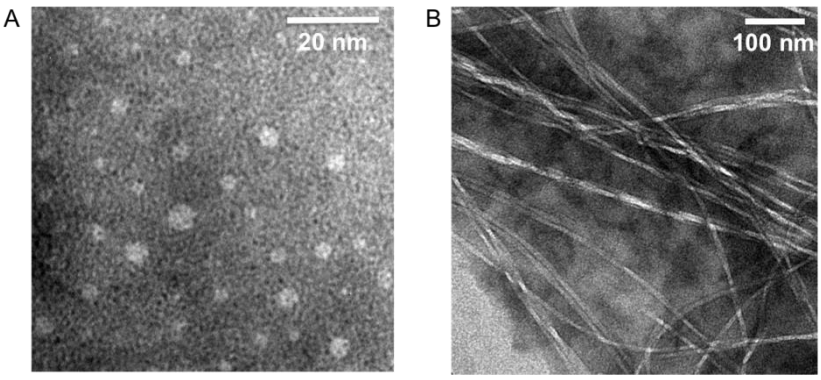

Figure 1: TEM images of lauryl-Gly-Gly-D-Ser-D-Lys-NH_2 at A) acidic B) alkaline pH.

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OR-54

Small electron-rich hole transporting materials for efficient perovskite solar cell

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Significant improvements in power conversion efficiency have been reported for solid-state solution-processed solar cells since the hybrid halide perovskite was introduced as active layer replacing the dye in the classical Dye Sensitized Solar Cells. To enhance Photo Conversion Efficiency (PCE) efficient Hole Transporting Materials (HTM) were designed to substitute the state-of-the art small molecule SpiroOMeTAD, since it implies complex synthesis and high cost.

Starting from this remarks, we synthetized two simple, triphenylamine-based, organic HTMs, namely H1 and H2, characterized by a symmetrical structure with a carbazole and a phenothiazine core unit, respectively. The choice of these core units, successfully used in organic optoelectronics [1,2], and the introduction of alkyl chains play an important role on the energy levels, molecular geometry and solid film self-assembly. Moreover H1 and H2 applied as HTM in photovoltaic devices achieve 14.3% and 13.2% efficiency, respectively, compared to the value of 14.8% obtained with the reference material SpiroOMeTAD.

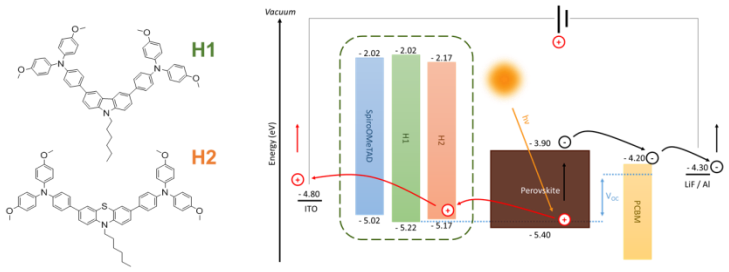

Figure 1: H1 and H2 structures and energy levels diagram.

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OR-55
Antibody powered DNA-based nanomachine

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Inspired from transport proteins, highly evolved machines that are essential to the crucial mechanism of cell transport we rationally designed here a new class of DNA-based nanomachines that can reversibly load and release a molecular cargo upon the binding to a specific target antibody. Our strategy to rationally design an antibody-driven DNA-based nanomachine involves the use of a triplex forming DNA strand that is designed to recognize a specific DNA strand through the formation of a clamp-like triplex forming mechanism that involves both Watson-Crick and Hoogsteen interactions and which is conjugated at the two ends with a pair of antigens [1]. Antibody binding to the two antigen tags in the nanomachine causes a conformational change that energetically disrupts the triplex-forming Hoogsteen interactions in the triplex complex thus destabilizing the nanomachine/cargo complex. The design principle for antibody-powered release of a molecular cargo strand is highly generalizable and can easily be adapted to other antibodies via the expedient of changing the recognition element employed. We have demonstrated here that our approach can be extended to different triggering antibodies and the effect can be specific and selective enough even in complex media (90% serum).

Given these attributes, the antibody-poweered DNA nanomachines we have developed here may prove of utility in a range of applications, including point-of-care diagnostics, controlled drug-release and in-vivo imaging.

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OR-56

Chiral oligothiophenes for optoelectronic applications: synthesis and spectroscopic study of supramolecular aggregation

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Nowadays, conjugated polymers and oligomers are widely used as organic semiconductors in optoelectronic devices such as field-effect transistors (OFET), light-emitting diodes (OLED) and solar cells (OPV) [1]; in particular, a very important role in this field has been played by thiophene-based systems. Their optical and electrical properties (structure of absorption bands, fluorescence efficiency, charge and exciton transport, etc.) depend not only on the chemical nature and the conformation assumed, but also on their supramolecular organization in the solid state [2]. The introduction of chiral groups in the chemical structure of conjugated systems represents a valid tool to drive their self-assembly.

We shall summarize our recent studies about the supramolecular aggregation for a set of new chiral conjugated oligomers, *ad hoc* designed and synthesized, consisting of an aromatic central ring (1,4-hydroquinone, 9*H*-carbazole, 1,4-diketopyrrolo[3,4-*c*]pyrrole and benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diol) functionalized with (*S*)-3,7-dimethyl-1-octyl groups and connected to two 2,2'-bithienyl units (Figure 1).

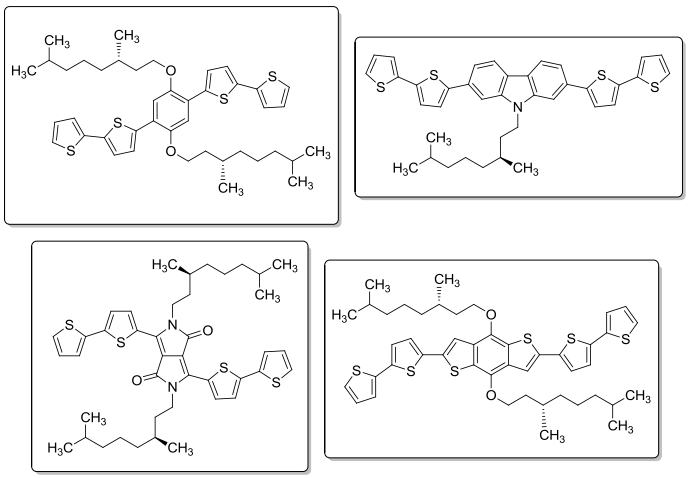

Figure 1: Chiral oligothiophenes synthesized and studied in this work.

In particular, we shall discuss: a) the synthetic route developed for the preparation of these new molecules; b) the investigation of their supramolecular self-assembly in solution and in thin films through optical (UV-VIS) and chiroptical (ECD) spectroscopies, in connection with optical microscopy analysis.

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Flash communications

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FL-30	Samuele STADERINI
FL-31	Vito A. TADDEO
FL-32	Stefano TOMMASONE
FL-33	Stefano VOLPI

FL-1

Achieving chiral electroanalysis on achiral electrodes in "inherently chiral" ionic liquid media

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Recently, "inherently chiral" electrodes have been introduced, of unprecedented enantiorecognition ability, able to both discriminate and quantify the enantiomers of chiral probes [1-2].

Now, to achieve chiral electroanalysis, an alternative strategy to using chiral electrodes is to work on achiral electrodes in a chiral medium. In this perspective chiral ionic liquids, CILs, should perform much better than chiral organic solvents, on account of their higher intrinsic order; and, by analogy with the electrode case, "inherently chiral" ionic liquids ICILs should perform better than CILs.

To obtain ICILs, the best strategy was to start from an alkylated bipyridine scaffold, 3,3'-bicollidine. In the last months enantiopure room-temperature ICILs have been obtained, and we have already highlighted their huge enantioselectivity, even as low-concentration additives in commercial achiral ionic liquids like $BMIMPF_6$.

The enantiomer peak separation is huge, comparable to that obtained working with inherently chiral electrodes. Importantly, similar and even better performances as low-concentration additives can also be obtained with smaller terms in the bicollidinium double salt series, solid at room T but of much easier synthesis. Moreover, enantiomer peak separation is modulated by the additive concentration, and the medium enantioselectivity holds with chemically different probes (even of applicative interest, like DOPA), or in the simultaneous presence of different probes.

Such results point to the possibility to obtain outstanding enantiodiscrimination on achiral electrodes employing the new compounds even as minority components in a commercial achiral medium.

Fondazione Cariplo, grant no. 2011-1851 "Inherently Chiral Ionic Liquids".

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FL-2

Structural changes of a doubly spin-labelled chemically driven molecular shuttle probed by PELDOR spectroscopy

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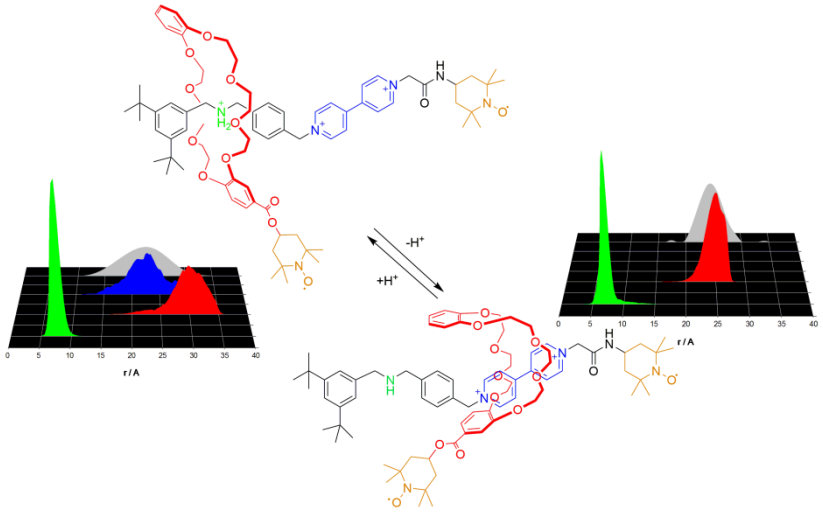
Gaining detailed information on the structural rearrangements associated with stimuli-induced molecular movements is of utmost importance for understanding the operation of molecular machines. Here pulsed electron-electron double resonance (PELDOR) was employed to monitor the geometrical changes arising upon chemical switching of a [2] rotaxane that behaves as an acid-base controlled molecular shuttle (Scheme 1). To this aim the rotaxane was endowed with stable nitroxide radical units in both the ring and axle components.[1] The combination of PELDOR data and molecular dynamic calculations indicates that in the investigated rotaxane the ring displacement along the axle, caused by the addition of a base, does not alter significantly the distance between the nitroxide labels but it is accompanied by a profound change in the geometry adopted by the macrocycle.



Scheme 1

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FL-3

Characterization of biosynthesized silver nanoparticles by voltammetry and scanning electrochemical microscopy

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Silver nanoparticles (AgNPs) have received a great attention recently, because of their distinctive physicochemical and biological properties. In fact, AgNPs are increasingly employed in various medical and consumer products, including household antiseptic sprays and antimicrobial coatings for medical devices that sterilize air and surfaces. Antibacterial AgNPs are known to dissolve and release Ag^+ ions under physiological conditions, and there has been much debate in the literature to establish if their reactivity arises due to an ionic or particulate effect, or both. To understand and predict how AgNPs behave in biological environments, it is essential considering the thermodynamics driving the dissolution of the material and how this phenomenon is related to the physicochemical properties of the particles and environmental conditions. Among the various factors that affect the dissolution process of the nanoparticles, the oxidation state of Ag in the AgNPs plays a relevant role. Therefore, investigation on the redox properties of silver particles and their reactivity at interfaces of various environments is highly desirable.

AgNPs can be prepared employing a variety of synthetic procedures, which are based on either chemical or biological approaches. Among them bio-production of AgNPs, using selected microorganisms, are very promising, as green methodologies. Recently, it has been reported that *Klebsiella oxytoca* (*KO*) cultures, treated with $AgNO_3$ solutions, are able to synthesize AgNPs, which are embedded in branched exopolysaccharides (EPS) (AgNPs-EPS). These materials could contain various forms of silver species and therefore could manifest different reactivity. These aspects can be studied profitably by using novel electroanalytical techniques, such as scanning electrochemical microscopy (SECM) and voltammetry. In this paper, we report a SECM-voltammetric investigation devoted at establishing the oxidation state and reactivity of AgNPs- EPS biosynthesized by a strain of *KO*, and evaluating the amount of Ag(I) released at the substrate/solution interface. Parallel voltammetric and spectroscopic (i.e., UV-Vis) measurements are also presented to prove the role of EPS, produced by *KO*, and the specific culture medium in the kinetics of the AgNPs formation and stabilization.

FL-4

Asymmetric synthesis of 3-amino-substituted isoindolinones via cascade hemiaminal-heterocyclization-intramolecular aza-Mannich reaction

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Isoindolinones are an important class of heterocycles found in various natural and synthetic biologically active compounds, with a large range of pharmacological applications for ex., in neurological disorders like Parkinson and Alzheimer diseases [1]. Therefore, much attention has been devoted to the development of new methods for the synthesis of 3-substituted isoindolinones, which constitute valuable structural scaffolds from a synthetic perspective [2].

Here we report the first asymmetric synthesis of 3-amino-substituted isoindolinones via cascade hemiaminal-heterocyclization-intramolecular aza-Mannich reaction of benzylamines and 2-formylbenzonitriles using chiral phase transfer conditions (PTC). A theoretical study of the enantioselective step provides a rationale for the mode of action of the best performing phase transfer catalyst and the observed face selectivity.

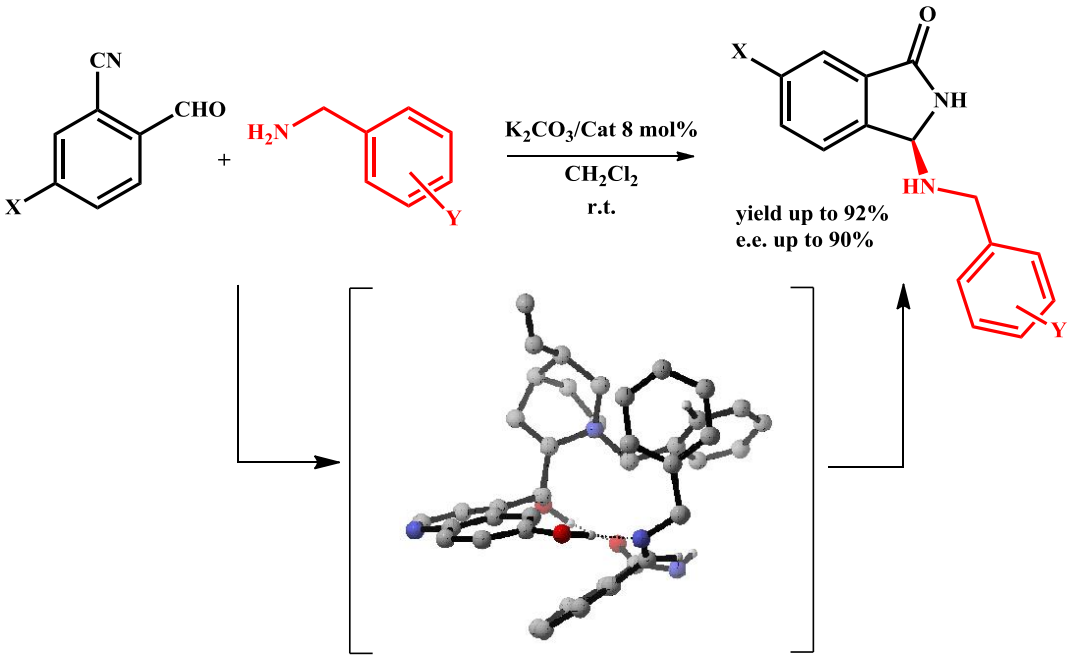

Figure 1: Synthesis of 3-amino-substituted isoindolinones.

[1] S. Dhanasekaran, A. Suneja, V. Bisai and V. K. Singh, *Org. Lett.* **18** (2016) 634-637.
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FL-5

Characterization of selected bentonite samples for aflatoxin adsorption

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A promising approach to protect animals against the harmful effects of mycotoxins contaminated feed is based on the use of feed additives. These additives are defined as substance that, when included into contaminated feed, can adsorb or denature mycotoxins in the digestive tract of animals thus reducing their absorption and carry-over in animal products. Since 2009, they are officially allowed in the EU as technological feed additives. Bentonite clays exhibit high adsorptive capacity for contaminants, including aflatoxin B_1 (AFB_1), a mycotoxin responsible for causing severe toxicity in several species including pigs, poultry and humans [1]. Recently, the use of bentonites as aflatoxin binder has been regulated (EU regulation No 1060 of 29 October 2013). Bentonites are composed predominantly of smectite, however, a wide variety of other minerals may occur as impurities, e.g. quartz, mica, feldspar, pyrite or calcium carbonate . The AFB_1 adsorption efficacy of a smectite depends strongly on its physical, chemical, and mineralogical properties. A correlation between physico-chemical properties of smectite and AFB_1 adsorption has not been established. The main objective of the present study was to identify potential effective smectites as AFB_1 adsorbents based on selection criteria. Specific objectives were 1) to compare physical, chemical and mineralogical properties of the smectites and correlate them with their AFB_1 adsorption efficacy, and 2) to study the effect of chemical activation of selected smectites on AFB_1 adsorption parameters. Briefly, 32 smectite samples were selected from industrial products or reference minerals. All smectites were analyzed against the published selection criteria for aflatoxin adsorbents: adsorption parameters (maximum adsorption capacity and affinity) determined by the method of adsorption isotherms, pH, cation exchange capacity (CEC), particle size distribution, and mineralogical and structural compositions. For the first time, it was observed a good correlation between the AFB_1 adsorption parameters and the geographical/geological origin of smectites. In addition, mineralogical and chemical analysis confirmed that some physical and chemical properties of smectites do have an influence on the AFB_1 sequestering capacity. Chemical activation of selected smectites did not improve their efficacy.

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FL-6

(*S*)-selectivity in phenylacetyl carbinols synthesis using the wild-type enzyme acetoin:dichlorophenolindophenol oxidoreductase from *Bacillus licheniformis*

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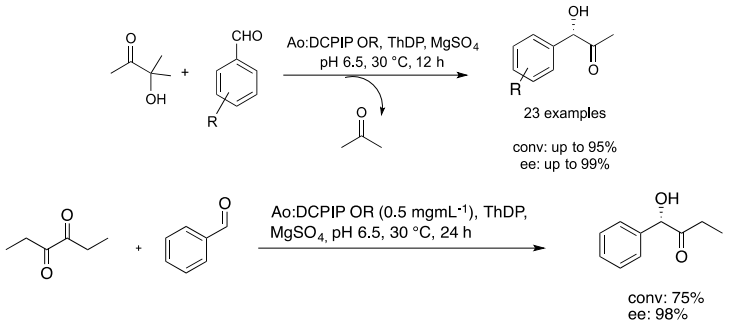
Thiamine diphosphate dependent enzymes are well known biocatalysts for asymmetric benzoin-type reactions leading to α-hydroxy ketones with preferential (*R*)-configuration. The pharmaceutically relevant (*R*)-1-hydroxy-1-phenylpropan-2-one, commonly known as phenylacetyl carbinol (PAC) has been synthesized using different ThDP-enzymes[1]. On the contrary, only few enzymatic carboligations affording (*S*)-PAC have been reported and all are catalyzed by variants of ThDP-dependent enzymes obtained through rational mutagenesis approaches [2]. Herein, we describe the enantioselective synthesis of (*S*)-PAC derivatives catalyzed by the wild-type acetoin:dichlorophenolindophenol oxidoreductase (Ao:DCPIP OR). (Scheme 1, reaction a). The cross-benzoin-like condensations of methylacetoin (acetyl donor) with differently substituted benzaldehydes proceed with complete chemoselectivity, yielding the target products with high conversion efficiencies (up to 95%) and good enantioselectivities (68-99%). Ao:DCPIP OR accepts hydroxy- and nitro-benzaldehydes as well as sterically demanding substrates, which are typically poor acceptors in enzymatic carboligations. In addition, the asymmetric synthesis of (*S*)-1-hydroxy-1-phenylbutane-2-one (phenylpropionyl carbinol) has been addressed using 3,4-hexanedione as propionyl donor (Scheme 1, reaction b) [3].



Scheme 1: Ao:DCPIP OR catalyzed synthesis of (*S*)-PAC (reaction a) and (*S*)-phenylpropionyl carbinol (reaction b).

[1] H. C. Hailes, D. Rother, M. Müller, R. Westphal, J. M. Ward and J. Pleiss, *FEBS J.* **288** (2013) 6374-6394.
[2] D.Rother, G. Kolter, T. Gerhards, C. L. Berthold, E. Gauchenova, M. Knoll, J. Pleiss, M. Müller, G. Scheider and M. Phol, *ChemCatChem* **3** (2011) 1587-1596.
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FL-7

Aqueous solar cells: novel trends in hybrid photoelectrochemical devices

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Dye sensitized solar cells (DSSCs) with high performances have been fabricated mainly with organic solvent-based liquid electrolytes. However, these solvents not only have high vapor pressure, but they are often toxic and flammable. In the last few years, the idea of moving towards a water-based or completely aqueous system clearly emerged [1].

DSSCs fabricated with aqueous electrolytes may offer reduced costs, non-flammability and environmental compatibility, but the presence of water in the cell may reduce the long-term stability as well as the photovoltaic performance. For this reason, in recent years, an increasing number of research articles has been published in this direction and new dyes, electrodes and electrolyte components are continuously proposed [2].

In this work, the study of different dyes as well as truly aqueous electrolytes is presented. A few curious and anomalous behaviors observed in the literature and in our laboratories are investigated for this class of electrolytes [3]. Moreover, the development of a series of novel aqueous gel electrolytes based on natural polymers is also discussed as well as their interesting photovoltaic characteristics

[1] F. Bella, C. Gerbaldi, C. Barolo, M. Grätzel, *Chem. Soc. Rev.* **44** (2015), 3431-3473.
[2] F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel, C. Gerbaldi, *Chem. Sci.*, **7** (2016) 4880-4890.
[3] S. Galliano, F. Bella, C. Gerbaldi, M. Falco, G. Viscardi, M. Grätzel, C. Barolo, *Energy Technol.*, just accepted.

FL-8

New calix[4]arene functionalised with Nile-Red and C_{60} for photoinduced electron transfer

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Electron transfer processes are ubiquitous in biological, physical, inorganic, and organic chemical systems. More relevant for our purpose is their implication in photosynthetic systems: after the absorption of a photon and the excitation energy transfer among the chromophores embedded in the antenna complexes, the excitation energy is funneled to the reaction center, where a charge-separation process occurs, generating an electron transfer cascade chain for the production of chemical energy.

In this context, our work is focused on the synthesis of two covalent electron donor-acceptor pairs and on the study of the photoinduced electron transfer occurring between the two chromophores. We chose 2-hydroxy Nile Red as the donor and fullerene C_{60} as the acceptor. Nile Red is a well-known fluorescent and solvatochromic dye, which has been used recently in the study of electron transfer with TiO_2 colloidal nanoparticles [1]. Fullerenes, on the other hand, are characterized by high electron affinity and require small reorganization energy in the electron transfer processes.

We anchored the two chromophores at the upper rim of a *cone* calix[4]arene (compound **1**), a convenient scaffold that allows the two moieties to be oriented in the same direction. Due to the residual flexibility of the structure, a modulation of the distance between the chromophores as a function of the medium could also be envisaged. The linear tri-components structure (**2**), composed by Nile Red-aromatic spacer-fullerene C_{60}, was also synthesized as a reference compound to study the influence of the calixarene scaffold on the electron transfer process.

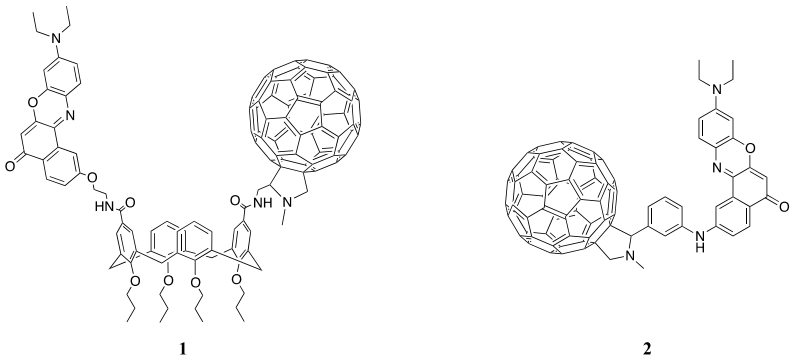

Figure 1: Target calix[4]arene **1** and reference compound **2**.

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FL-9

POLìPO: bio-polymers from vegetable oils

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In 2013 in the world there were produced 250,000,000 tons of plastics with drastic effects on the environment. Forecasts say that by 2050 the plastic dispersed in the sea will have a mass greater than the mass of acquatic living organisms [1].

Polìpo aims to the development of plastic materials from renewable and biodegradable resources. Our proposal involves the use of fats and oils as a raw source for the production of fully biodegradable polymers featuring a structure similar to polyhydroxyalkanoates (PHA). The production and polymerization of PHA with a totally chemical route is an innovative approach if compared with the current industrial production because it represents the first non-fermentative process known today. One of the most important factors is the possibility to vary the composition of the material produced, changing process parameters in contrast with classic ways where it is necessary to work with specify bacteria in very controlled conditions.

Moreover it would be the first industrial production process of production of a polyester from unsaturated fatty acids.

Polìpo's process provides many advantages compared to a traditional process of PHA/PHB production such as: flexibility, low volume production, complete transformation of the reagents into products, higher purity of the products without extractions, lower costs.

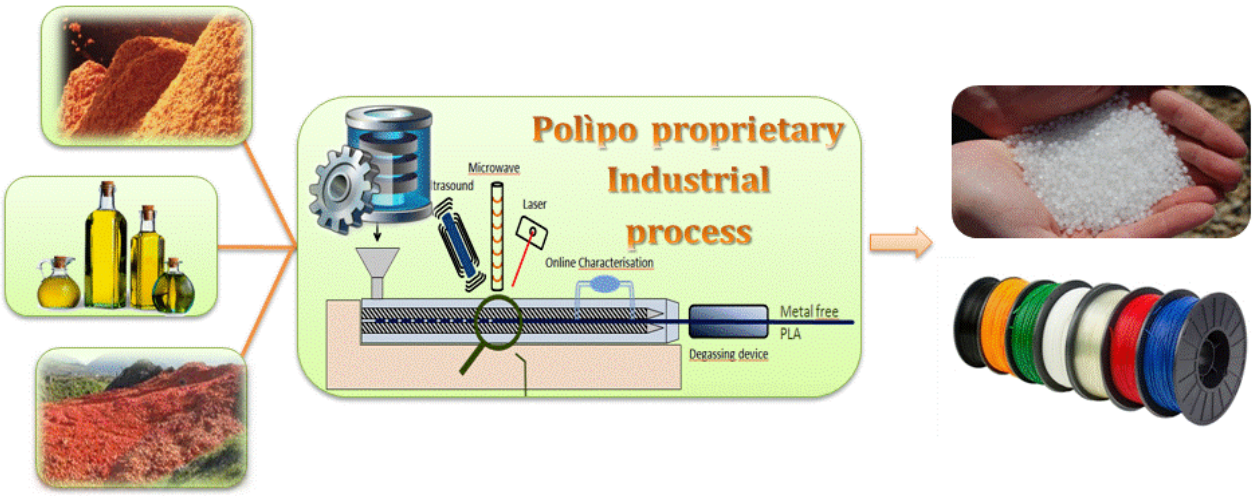

Figure 1: Process scheme to transform waste into pellet or filament.

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FL-10

UHPLC-PDA analysis of five antibiotics in human plasma using air-assisted dispersive liquid-liquid microextractiom with solidification of the floating organic droplet (AA-DLLME-SFO)

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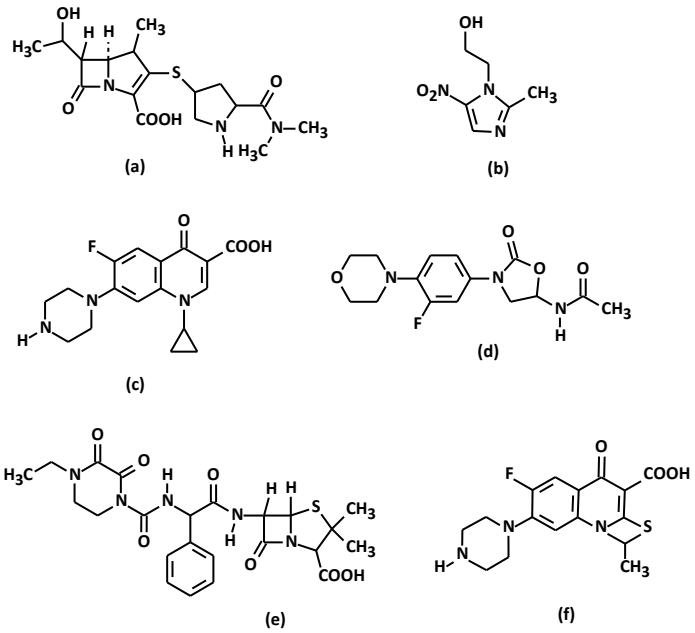
The increase in the incidence of drug-resistant *Gram-positive* pathogens (*e.g. Staphylococcus aureus*) or *Gram-negative (e.g. P. aeruginosa)* has created a great challenge in the treatment of patients with serious infections [1]. To prevent the multidrug resistance an antimicrobial combination therapy may be used. Recent trends in sample preparation are clearly towards miniaturization, automation, high-throughput performance, on-line coupling with analytical instruments and cost-effectiveness through extremely low or no solvent consumption.



A new microextraction method was developed using extracting solvents which have density lighter than water integrated with the solidification of the organic floating drop (DLLME-SFO) [2]. The extractant solvent may have some requirements: Immiscibility with water, low density, low toxicity and a melting point around room temperature. In the present work , two sample preparation techniques (PP and AA-DLLME-SFO) were combined for the determination of meropenem, metronidazole, ciprofloxacin, linezolid and piperacillin in human plasma by UHPLC-PDA. This combination not only resulted in a high enrichment factor but also offered numerous advantages such as simplicity, ease of operation, low detection limits, short analysis time using extraction solvent with lower toxicity instead of highly toxic solvents.

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FL-11

Identification of IgY with electrochemical immunosensor

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It has been recently demonstrated that chicken egg-yolk immunoglobulin Y (IgY) has many immunological properties not only on avian, but also on mammalians, such as human [1]. Since it is easy to insulate (directly from egg yolk – where it is present at a concentration of 10 mg/mL), recently scientists proposed new immunotherapies based on the addiction of IgY to medicine or food both for animals and humans [1]. In addition, eggs are very common ingredients in all diets, so it is important to understand if it is possible to obtain such immunological properties from every day foods, or if IgY degrades during cooking procedures and temperature changes.

For this reason, we developed an electrochemical immunosensors based on Au-nanoelectrodes ensemble (NEE) as transducer, able to identify IgY in different matrices. NEEs are prepared via template electroless deposition of gold in a polycarbonate (PC) membrane. Polycarbonate is affine to proteins and antibodies and, for these reason NEEs are very suitable to be used both as electrodes and as protein-receiver material [2]. IgY, the biological molecular recognition element, is immobilized directly on the PC surface of the electrode (Fig. 1 – left). It is recognized by the secondary antibody anti-IgY labelled with HRP, an electroactive enzyme that reacts with his substrate (H_2O_2) and a redox mediator (methylene blue), originating the electrocatalytic cycle shown in Fig. 1 – right.

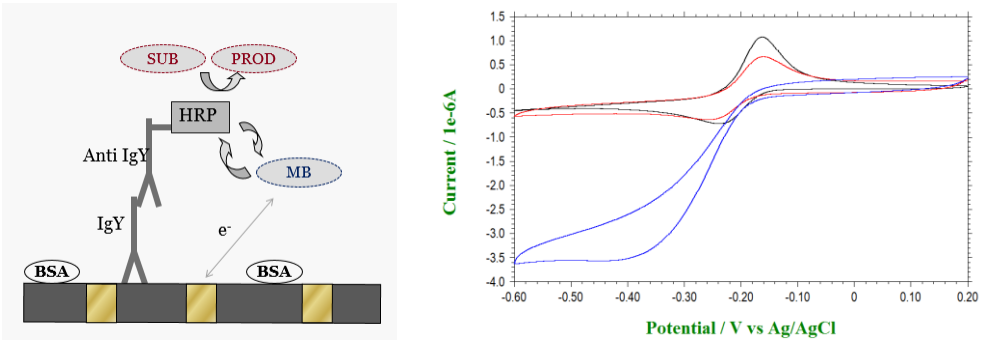

Figure 1: Scheme of the immunosensor (left) and voltammetric behavior (right).

The proposed immunosensor was tested to identify of IgY in egg samples and in lyophilized eggs used as food integrator for sportsmen. Electrophoresis and western blot were applied to confirm the results obtained with the sensor.

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FL-12

Mimicking collagen ageing by chemical cross-linking and preliminary biological evaluation

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Due to ageing, human tissues undergo several alterations in their functions, including susceptibility to injury and reduced healing capacity. The most important structural proteins found in the extracellular matrix (ECM), such as collagen and elastin are usually strongly involved. Collagen is a trimeric protein containing two α1, and one α2 chains each of about 1000 amino acids. It is known that during ageing type I collagen becomes more stiff and less flexible, impairing maintenance and degradation of the ECM; these mechanical modifications are probably due to the accumulation of non-enzymatic crosslinks affording several products known as Advanced Glycation End-products (AGEs) [1]. The natural low biological turnover of collagen makes it particularly susceptible to interaction with metabolites, primarily glucose causing non-enzymatic crosslinks. Moreover besides the elderly, people who suffer of type II diabetes are particularly affected by AGE cross-linking [2]. To date, the role of collagen glycation is not fully understood and therefore it needs to be further investigated. In particular there are two different aspects that are crucial in physio-pathological states. One are the biomechanical effects of intermolecular cross-linking that involves an alteration of structural proprieties of this protein. The second aspect is related to the bio-signalling role of collagen. Glycation of specific amino acid could lead to the dramatic modification of the interaction of collagen with other biomolecules. Here we present a preliminary work where we try to mimic the non-enzymatic cross-link of collagen and the effect on chondrocytes. Collagen was chemically modified using 1,4-Butanediol diglycidyl ether (**BDDGE**) or Methylglyoxal (**MeG**) as cross-linking agents [3]. The modified collagen scaffolds have been used as supports for human immortalized C28 chondrocytes. The cells grew on all three scaffolds with a comparable duplication time. Furthermore, the cell morphology has been observed by confocal microscope and it has been noted that cells grown on BDDGE scaffold exhibit long and thin protrusions that could be tunnelling nanotubes (TNT).

[1] M. Brennan, *J. Biol. Chem.* **264** (1989) 20947-20952.
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[3] A. Papoulis, A. Yousef and R. Bucala, *Biochem.* **34** (1995) 648-655.

FL-13

Application of a structure based virtual screening strategy for the identification of new human lactate dehydrogenase 5 inhibitors

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Inhibitors of human lactate dehydrogenase isoform 5 (hLDH-5) are considered promising therapeutic agents against cancer, since the enzyme was found to be overexpressed in most invasive cancer cells and showed to be linked to their vitality, especially under hypoxic conditions. Human LDH-5 is composed of the tetrameric association of four LDH-A subunits and catalyses exactly the reduction of pyruvate to lactate, a crucial step in the anaerobic glycolysis. Therefore, this enzymatic subtype affected the reduction of the conversion of glucose to lactate and the consecutive starvation of cancerous cells. Furthermore, no significant side effects or clinical symptoms have been reported subsequently to the enzyme inhibition, except for myoglobinuria upon intense physical exertion, thus increasing the validity of hLDH5 as anticancer target.

In order to identifying new hLDH5 inhibitors, a virtual screening (VS) platform based on multiple receptor-based pharmacophore searches has been developed and applied to filter the Asinex Gold and Platinum database, comprising about 320,000 commercially available compounds. Closed and open conformational states of hLDH5 have been reported in literature and several X-ray crystal structures of the enzyme bound to inhibitors have been deposited in the Protein Data Bank. Thus, three different pharmacophore models were generated. In particular, the crystal structure of hLDH5 in complex with oxamate and the coenzyme NADH (PDB code 1I10), and the malonic derivate AZ-33 (PDB code 4AJP), respectively, were used to build the first and second pharmacophore hypothesis. For the third model, the structure of the previously developed N-hydroxindol-2-carboxilic acid complexed with an open loop conformation of the enzyme was employed [1]. Furthermore, to refine the screening, docking studies performed by using the ChemScore fitness function of GOLD and followed by molecular dynamic (MD) simulations were carried out. The top ranked compounds were experimentally test for their inhibition activity toward hLDH5 and enzymatic assays showed that, among the ten selected compounds, two proved to inhibit the enzyme activity with Ki values lower than 100 μM.

[1] C. Granchi, S. Roy, C. Giacomelli, M. Macchia, T. Tuccinardi, A. Martinelli, M. Lanza, L. Betti, G. Giannaccini, A. Lucacchini, N. Funel, L. G. Leon, E. Giovannetti, G. J. Peters, R. Palchaudhuri, E. C. Calvaresi, P. J. Hergenrother and F. Minutolo, *J. Med. Chem.* **54** (2011) 1599-1612.

FL-14

Aqueous self-assembly of short peptides containing Norbornene amino acid

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Many papers report on spontaneous assembly of peptides into ordered nanostructures with a variety of morphologies and this number is still expanding [1], nevertheless some limitations are well-known such as a low stability in biological medium and their unstable conformation especially when they are short or medium-sized. The insertion of unnatural amino acids in the peptide sequences is a well-known tool to overcome these problems; in particular, the group of Cα,α-tetrasubstituted residues, in which the quaternary α-carbon is part of a ring has been the object of extensive investigation [2]. On the other hand, studies on the self-assembly of short peptides containing cyclic Cα-tetrasubstituted amino acids are very rare.

The two diastereoisomeric pentapeptides AcAla-NRB-Ala-Aib-AlaNH$_2$ **1** and **2**, containing the two enantiomers of the non-proteinogenic Cα-tetrasubstituted norbornene amino acid (NRB) were synthesized and studied [3]. Interestingly, despite they are made of hydrophobic amino acids, they resulted insoluble in organic solvent, but completely soluble in water. The formation of supramolecular assemblies in water was assessed by TEM and DLS and the stability of the aggregates in fetal bovine serum was also evaluated. Conformational analysis on **1** and **2** were performed to gain insight on their secondary structures.

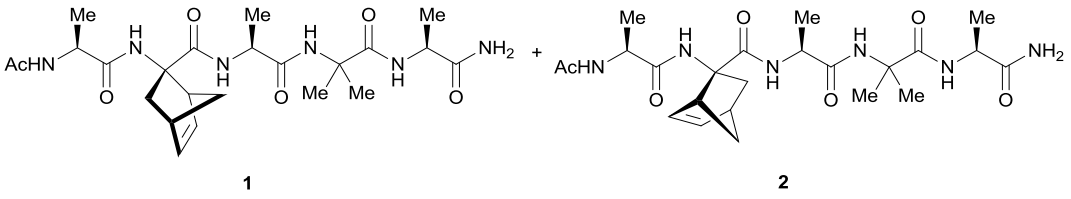

Figure 1: Pentapeptides AcAla-NRB-Ala-Aib-AlaNH$_2$ containing the two enantiomers of norbornene amino acid (NRB).

[1] C. Aleman, A. Bianco and M. Venanzi, "Peptide materials: From nanostructures to applications", Wiley-VCH, 2013, ISBN: 978-1-119-95373-9.
[2] C. Toniolo, M. Crisma, F. Formaggio and C. Peggion, *Biopolymers* **60** (2001) 396-419.
[3] A. Ruffoni, M. V. Cavanna, S. Argentiere, S. Locarno, S. Pellegrino, M. L. Gelmi and F. Clerici, *RSC Adv.* **6 (**2016) 90754-90759.

FL-15

Porphyrin conjugated SiC/SiO_2 nanowires for X-ray-excited photodynamic therapy

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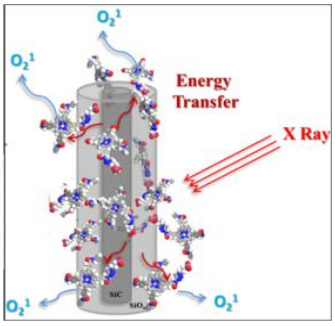
In the last decade, an increasing attention was devoted to the preparation of nanosystems for biomedical applications, in particular for cancer treatment, such as photodynamic therapy (PDT).

Here we report the preparation of a novel nanosystem based on *core-shell* SiC/SiO_2 nanowires conjugated with porphyrins for application in photodynamic therapy.

Recently we evidenced that 3C-SiC/SiO_2 nanowires can easily penetrate the cell membrane and that they are cytocompatible [1]. Porphyrins are photosensitizers largely employed in PDT, absorbing light and producing cytotoxic singlet oxygen. We designed to conjugate porphyrins to the SiC/SiO_2 nanowires to obtain a nanosystem able to promote X-ray-excited PDT for deep tumour treatment [2]. In this communication we present a new conjugation strategy based on the formation of amide bonds between *tetra*(4-carboxyphenyl)porphyrin (H_2TCPP) and the nanowires, under very mild conditions. Short hydrophilic PEG chains were synthesized and linked to the porphyrins to increase the dispersion of the nanosystem in a biological medium.



The hybrid nanosystem was characterized by fluorescence spectroscopy, that evidenced the successful porphyrin conjugation. In vitro studies on tumour cell lines were carried out and the antiproliferative activity of the nanosystem was proved.

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[2] F. Rossi, E. Bedogni, F. Bigi, T. Rimoldi, L. Cristofolini, S. Pinelli, R. Alinovi, M. Negri, S. C. Dhanabalan, G. Attolini, F. Fabbri, M. Goldoni, A. Mutti, G. Benecchi, C. Ghetti, S. Iannotta and G. Salviati, *Sci. Rep.* **5** (2015) 7606-7611.

FL-16

Gold nanoparticles functionalized with cyclic γ-aminoproline RGD peptide for selective $\alpha_v\beta_3$ integrin targeting

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Integrin $\alpha_v\beta_3$ is a cell-adhesion molecule involved in angiogenesis, tumor invasion and metastasis which is overexpressed by endothelial tumor cells as well as tumor neovasculature. The most potent $\alpha_v\beta_3$ ligands are cyclic peptides containing the RGD sequence opportunely functionalized with multivalent scaffolds. Gold nanoparticles (AuNPs) are ideal platforms for targeting $\alpha_v\beta_3$ integrins and could be exploited for tumor diagnosis and for therapeutic purposes in theranostic formulations.

We have developed novel PEGylated AuNPs [1] functionalized with cyclic-aminoproline RGD peptides (cAmpRGD) [2] which show high affinity and selectivity for $\alpha_v\beta_3$ integrins. In this contribution we will discuss the molecular design, the preparation and characterization of these nanoparticles. Furthermore we will show their excellent targeting properties from data collected using the human melanoma cell line M21 which overexpress integrin $\alpha_v\beta_3$. In fact, cAmpRGD-AuNPs target M21 cells 4 times more efficiently than control AuNPs, selectively inhibit cellular adhesion to vitronectin (the natural, RGD containing ligand) by 50% at 1 nM concentration, and do not show any significant toxicity at concentrations as high as 10 nM after 24 h as demonstrated by Annexin V/ PI staining assays and no significant alterations of the cell cycle. In view of these characteristics we are working on developing cAmpRGD-AuNPs as novel microSPECT/CT tracers for diagnostic imaging [3].

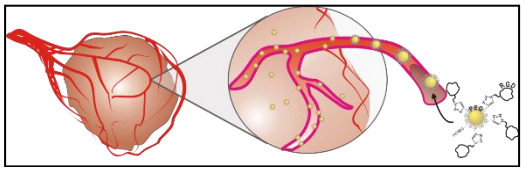

Figure 1. Schematic representation of tumor targeting by PEGylated RGD-AuNPs.

[1] L. Maus, O. Dick, H. Bading, J. P. Spatz and R. Fiammengo, *ACS Nano* **4** (2010) 6617-6628.
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FL-17

Mixed CuNi oxide-graphene nanocomposite microspheres as anode for energy storage devices

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Transition metal oxides (TMOs = Fe, Ni, Cu, Ti, etc.) have been intensively studied as anodes materials in lithium ion batteries (LIBs) due to their higher reversible capacities compared with commercial graphite. Nevertheless, these materials are affected by strong volume variations upon insertion/extraction of Li^+ ions that leads to the rapid destructuration of the electrode often resulting in dramatic irreversible capacity loss and poor cycling stability [1].

The synthesis of TMOs in different nanostructures is an attractive solution [2]. In addition, by opportunely coupling the positive characteristics of nanostructured TMOs with graphene sheets (GNS) enhanced material stability and greatly improved electrochemical performances can be achieved.

In this work, we present our recent results on the development of 3D/2D mixed CuNi oxide-graphene composite (CNO/GNS) mesoporous nanoparticles used as anode, along with the structural/morphological and electrochemical characterization thereof. The data are compared with pristine CNO sample demonstrating the remarkable performance improvement of the composites.

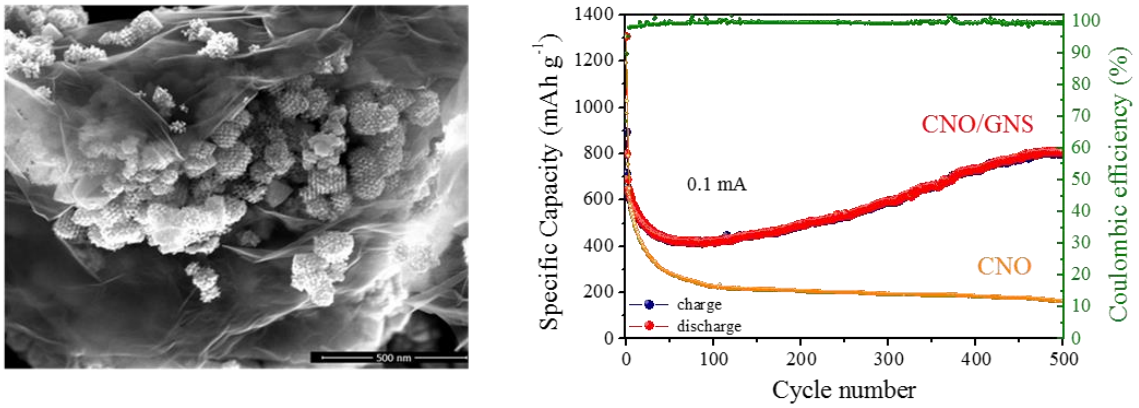

Figure 1: FESEM image of CNO/GNS and galvanostatic cycling behavior of CNO/GNS compared with CNO without graphene (CNO = mixed Cu-Ni oxide).

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FL-18

Antioxidant activity of new tetrahydroberberine analogous

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Tetrahydroberberine (THB) is an alkaloid extracted from *Corydalis ambigua*; it has significant pharmacological activity that differs from the parent berberine (BB).

In contrast to the cytotoxic effects of berberine, tetrahydroberberine has been reported to show little cytotoxicity toward several lines of cells, but instead to be effective as an antioxidant [1].

On the basis of these considerations, and as part of our program aimed at developing new strategies for the construction of potential biologically active compounds from 1,2-diaza-1,3-dienes (DDs) [2], we wish to report an efficient synthesis of THB analogous form DDs **1** and dihydroberberine (DHB) **2**.

As summarized in Figure 1, in the first step, a Michael addition of the enamine group of DHB **2** to the azo-ene system of DD produces the zwitterionic hydrazone adduct intermediate **3**. Subsequently, an intramolecular azacyclization via CH/NH tautomerization leads to the formation of THB analogous **4**.

We also tested the antioxidant capacity of these products (**4**) with an ORAC test, the analogous show an high antioxidant capacity, connected to the reducing power against the peroxide radical ROO.

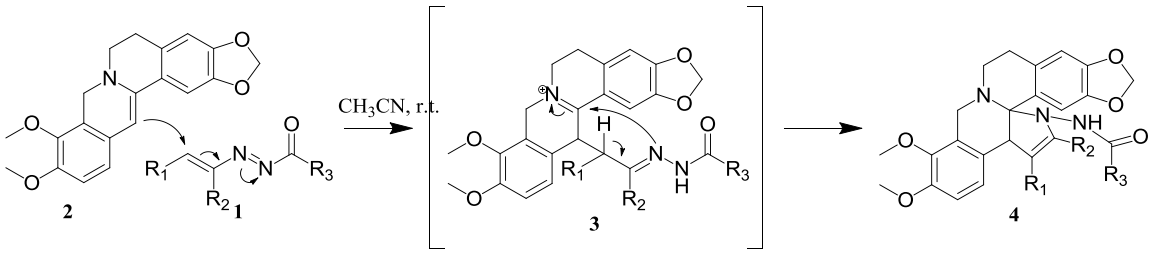

Figure 1

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FL-19

Poly(ethylene glycol)s as grinding additives in the mechanochemical preparation of highly functionalized 3,5-disubstituted hydantoins

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Poly(ethylene glycol)s (PEGs) are eco-friendly solvents [1], that have a positive influence as grinding agents for the mechanochemical preparation of compounds with high interest in fine chemistry and pharmaceutical chemistry [2].

Effects of poly(ethylene glycol)s PEGs, in the mechanochemical synthesis of highly functionalized 3,5-disubstituted hydantoins were tested in several conditions and compared with the dry-grinding conditions.

The results showed that the PEGs have an influence in the hydantoins synthesis, the quantity or the molecular weight of the PEGs also influenced the yield of the reaction.

Compared to dry-grinding procedures, grinding assisted procedure showed cleaner reaction profiles.

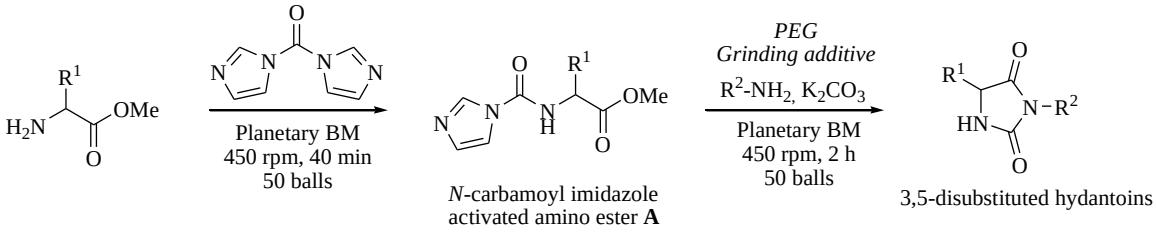

Figure 1: Scheme of reaction.

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FL-20

Study of human aldehyde oxidase metabolism towards aza-aromatic oxidation and amide hydrolysis

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One of the major challenges for pharmaceutical companies is knowing the metabolism of drug candidates in the early stages of drug research. Cytochrome (P450s) are the main enzyme group examined during metabolism studies, but interest in Aldehyde Oxidase (AOX) has increased in recent times [1]. AOX is a metabolic enzyme able to oxidase the aldehyde functionality into the carboxylic acid and also aza-aromatic compounds with the addition of one oxygen atom to the ring. This latter reaction is very important in drug development because many drugs contain aza-aromatic scaffold. Furthermore, recently it has been discovered that AOX also hydrolyzes amide compounds with the production of the corresponding amine [2].

The study herein reported is based on the expansion of the chemical space of commonly used drugs and drug candidates; several aza-aromatic and amide compounds (Figure 1) were acquired or synthesized to assess whether or not they were oxidised by AOX by *in vitro* assays. The studies covered a wide variety of different scaffolds with *N*-aromatic and amide compounds. In addition, we also tested aromatic compounds with the same scaffold but with different substituents in different positions in aromatic ring.

The obtained results could help medicinal chemists design drugs with a reduced risk of failure due to AOX-mediated metabolism. Eventually, these findings can be also used to generate *in silico* models for metabolism prediction.

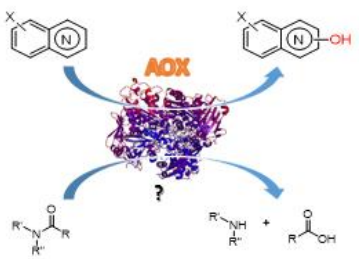

Figure 1. Studied AOX reactions.

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FL-21

2-hydroxyimino-aldehyde: synthesis and characterization of new compound with high versatility

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2-hydroxyimino-aldehydes (Figure 1) are a class of organic molecules that offers high functional versatility. Their structure, in which there is an aldehyde group adjacent to an oxime group, endows them with some interesting proprieties, such as an unusually low pKa compared to simple oxime molecules and the existence of two configurational isomers E and Z. It is also possible to change the relative population of isomers E and Z through photostimolation and then to study the time of thermal relaxation. Furthermore, the aldehyde group can bind bioactive molecules and the oxime group may possess antibacterial and anticancer properties.

The synthesis of 2-hydroxyimino-aldehydes is a very simple reaction that involves α-oxymation of aldehydes using cheap and common reagents [1]. In this work we study the chemical and physical properties of this class of molecules in order to use them in different applications as photochemical probes, enzyme inhibitors, toxic metal ligands, amphiphiles for liposomes preparation and stimuli-responsive monomers.

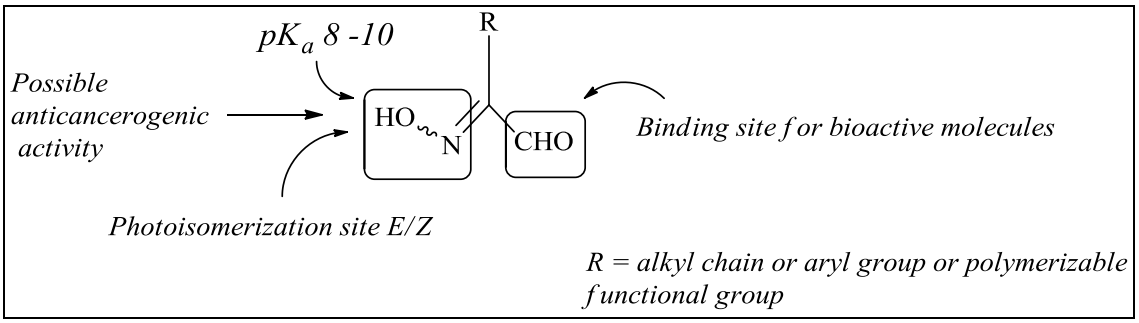

Figure 1: 2-hydroxyimino-aldehyde.

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FL-22

Enantiopure C1-symmetric N-heterocyclic carbene ligands for olefin metathesis ruthenium catalysts

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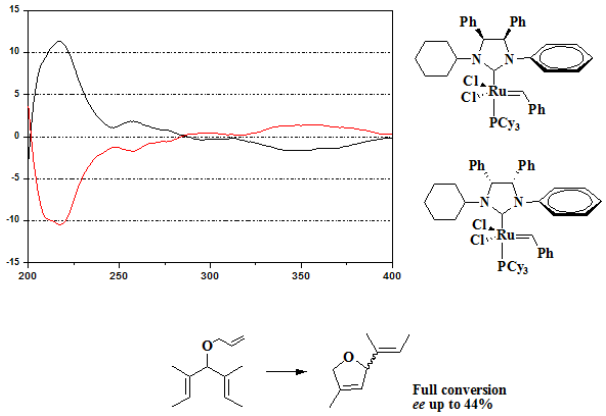
Catalytic olefin metathesis has emerged in the past decades as a very powerful tool for the formation of new carbon-carbon multiple bonds [1]. Due to their high stability, easy-handling and versatility ruthenium-based catalysts bearing N-heterocyclic carbene (NHC) ligands are widely applied in olefin metathesis.

Among all metathesis transformations, very important are the asymmetric metathesis reactions which transform prochiral olefins in enantio-enriched alkenes [2]. For this reason is nowadays very interesting to obtain enantiomerically pure catalysts which are active, selective and easy to synthesize. One of the most used strategies consists in coordinating to the metal an optically active NHC but, unfortunately, this route implies the use of optically active starting materials which are often very expensive and difficult to reach.

In this contribution we present a very original synthetic approach which led to obtain a chiral NHC from a meso diamine by separating the racemic mixture using chiral high pressure liquid chromatography (HPLC). Two optically active catalysts have been obtained and tested in some of the most common asymmetric metathesis transformations showing an encouraging enantioselectivity. Enantiopurity of the complexes has been supported by circular dichroism spectra and absolute configuration has been assigned using DFT calculations.



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FL-23

Strategies for generation and trapping of highly reactive fluorocarbenoids

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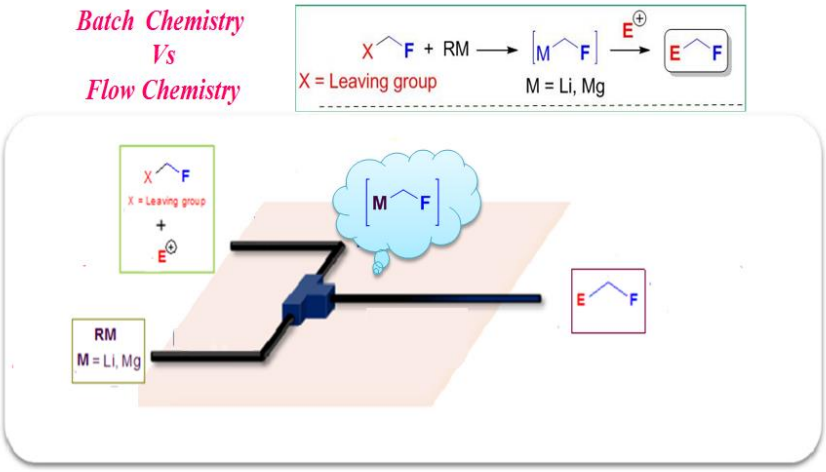
Fluorinated compounds have attracted a great deal of interest by the scientists involved in many field of science and technology. The selective introduction of monofluoromethyl groups into small organic molecules remains still a challenge. In this context, fluoromethylation strategies – i.e. the incorporation of a preformed C-F building block – is highly attractive because it allows to access valuable fluorinated scaffolds through a simple synthetic operation [1]. Unlike the extensive use of different halocarbenoids in organic synthesis [2], very few precedents can be found into the literature for fluoroalkyllithium or fluoroalkylmagnesium reagents. Hammerschmidt reported very recently the generation of fluoromethyllithium by a tin-lithium exchange strategy [3]. However, despite the configurational stability, the pronounced chemical instability severely limited its use in synthetic processes. We addressed these issues by employing α-fluorosulfoxides as fluoro-carbenoidic precursors. Mechanistic rationales and applications will be presented.



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FL-24

Visible light photocatalytic transformation of α,β-unsaturated-*N*-tosylhydrazones: a novel route to allylic sulfones

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N-Tosylhydrazones have been classically exploited for the generation of lithioalkenes and non-stabilized diazo, while recently they have been employed as reagents in palladium catalyzed cross couplings [1]. Moreover, their ability to generate *N*-centered hydrazonyl radicals was demonstrated and used to assembly nitrogen-containing heterocycles [2].

During our investigations on new transformations involving conjugated tosylhydrazones, we observe that no intramolecular hydroamination of the double bond took place under photoredox conditions. An allylic sulfone was recovered as the only product, obtained through nitrogen loss and a formal transposition of the tosyl group.

Reaction conditions were optimized in terms of base, solvent and catalyst using crotonaldehyde tosylhydrazone as model substrate. The scope of the reaction was also evaluated by using different arylsulfonylhydrazones and was observed that substituents on both the phenyl ring and the aliphatic chain are tolerated, affording the corresponding allylic sulfones in moderate to good yields (Figure 1). Finally, experimental and theoretical approaches were combined to gain some insight into the mechanism of the reaction. In particular, luminescence-quenching experiments, capture of radical intermediates with TEMPO and employment of isotopically marked solvents, together with a kinetic study, they all indicate a vinyl radical as key intermediate.

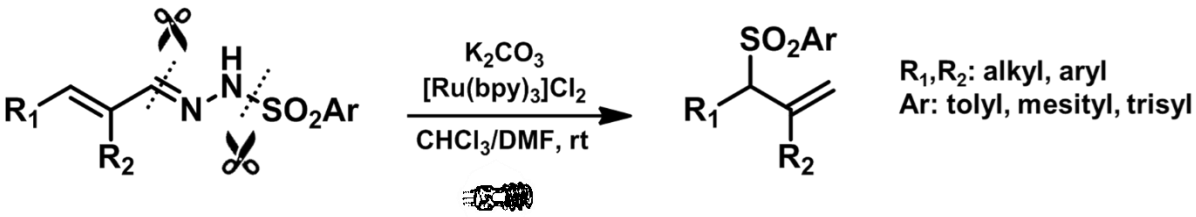

Figure 1: Synthesis of allylic sulfones from conjugated tosylhydrazones.

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FL-25

Tailoring the surface properties of TiO_2: shape controlled nanoparticles for the optimization of functional properties

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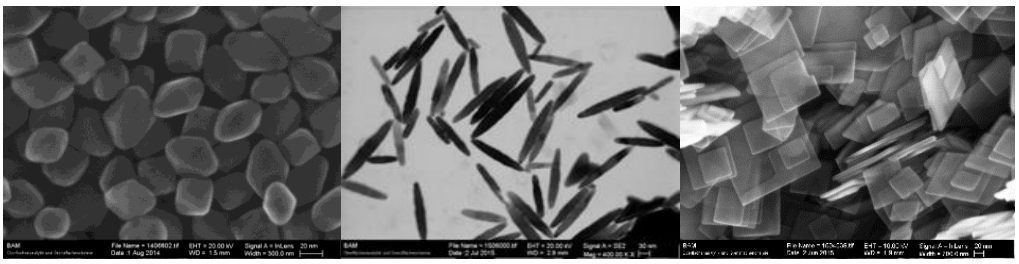
The synthesis of TiO_2 nanoparticles (NPs) with well-defined morphology and size is fundamental for the development of advanced nanomaterials in various application fields: photocatalysis, photovoltaics, sensors, bone-implants with enhanced bone integration. Synthetic routes were developed for bipyramidal TiO_2 facet-controlled anatase NPs with low truncation along the c-axis and acicular morphology, through hydrothermal treatments of aqueous solutions of Ti(IV)(triethanolamine)$_2$ [1,2]. The formation of anatase (101) surfaces is favoured by the presence of OH ligands, including water. Therefore, the shape control agents used were pH and triethanolamine. Bipyramidal TiO_2 anatase NPs with low truncation along the c-axis and with dimensional polydispersity in the 5-20% range were produced, along with the procedure and the process parameters (pH, temperature and reagents concentrations) to modulate the NP size along the c-axis in the 20-60 nm range. Through a careful experimental design the influence of many process parameters (pH, temperature, shape controller type and concentration) on the synthesis outcome (size, shape and polydispersity), a predictive soft model was developed. The model is able to predict reasonably well the synthesis outcome. Synthesis of TiO_2 anatase nanoplatelets are carried out with a solvothermal synthesis using Titanium (IV) Butoxide [3]. Concentrated hydrofluoric acid as capping agents.



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FL-26

^{13}C NMR Spectroscopy as valuable alternative for the $\delta^{13}C$ determination of carbonates

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The growth in level of carbon dioxide in the atmosphere raises much interest in the chemical and physical implications of carbon sequestration. One of the most promising storage mechanisms is geological sequestration, where the captured CO_2 is pressurized and pumped deep underground into geological formations [1]. The study of mineralization reactions of CO_2 has other benefits in addition to helping in evaluate the safety of geological sequestration proposals. Most studies on mineral carbonation reactions have focused on reactivity in aqueous solution, identification and characterization reaction products and kinetics. Stable isotope analyses provide a powerful tool to trace the source and the fate of CO_2 in the subsurface, as shown by several studies [2]. The isotopic analysis is an useful methodology to asses information related to the medical, biological and geographical features of materials. The highly sensitive (up to 0.01‰) technique based on isotope ratio mass spectrometry (IRMS) is the method of choice for the ^{13}C measurements in terms of $\delta^{13}C$. However, several methods for isotopic analysis have been reported as LARA (Laser-Assisted Ratio Analyzer), OGE (Optogalvanic Effect), NDIRS (Non-Dispersive Infrared Spectroscopy) and traditional IR. In such scenario, great interest is devoted to the development of new analytical methodologies in order to increase the choice of the analyst. Most studies on mineral carbonation reactions have focused on reactivity in aqueous solutions and in situ NMR spectroscopy method possesses the ability to monitor the chemical evolution of CO_2 in the same conditions of geological CO_2 sequestration [3]. The aim of this study is an innovative use of ^{13}C NMR spectroscopy to the direct determination of total carbon isotope ratio of carbon at natural abundance.The results assess the agreement and the reliability of ^{13}C NMR technique for the measurement of carbon stable isotope ratio in comparison to IRMS.

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FL-27

Quinine-catalyzed atroposelective biaryl coupling

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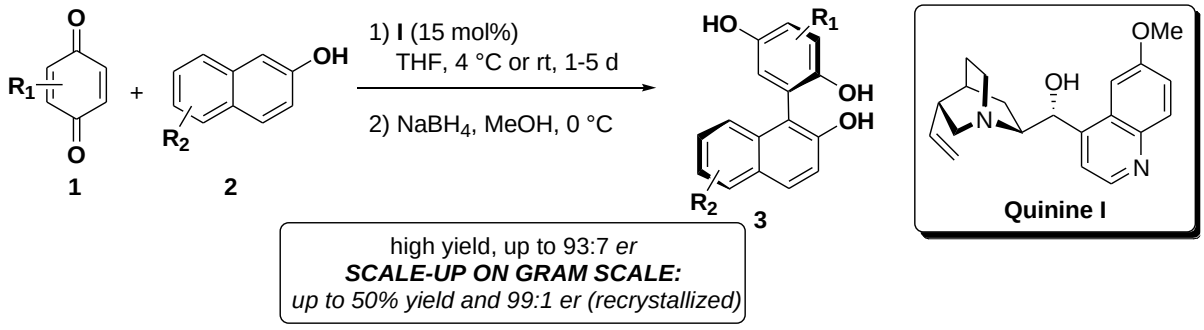
Biaryl moieties bearing a chiral axis are present in a number of natural products and are widely exploited in asymmetric catalysis [1]. However, the large scale synthesis of these molecules suffers from some issues which are critical for industry, such as the employment of transition metals and oxidants or the need to resolve racemic products, with a maximum theoretical yield of 50%. Therefore, an efficient organocatalytic approach to prepare these compounds could represent a major breakthrough [2]. In this work we report an organocatalyzed C(sp^2)-C(sp^2) coupling between 2-naphthols **2** and 1,4-benzoquinones **1**, catalyzed by the simple *Cinchona* alkaloid quinine and leading to axially chiral molecules **3** which closely resemble the skeleton of binaphthols (Scheme 1) [3].



Scheme 1. Organocatalyzed asymmetric addition of quinones **1** to naphthols **2**.

In order to ensure smooth reactivity and hindered rotation along the newly formed C-C bond, halogenated quinones were employed (R_1 = Cl, Br). 2-Naphthols substituted with bromine or methoxy group in different positions or unsubstituted afford the product in high yield (up to 99%) and good enantioselectivity (*er* up to 93:7). The scale-up of the process on gram scale was developed, leading to nearly enantiopure products upon recrystallization.

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FL-28

Flexible dye-sensitized solar cells based on titanium grids and polymeric electrolyte

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Dye Sensitized Solar Cells (DSSCs) gather great interest for the possibility of different applications such as architectural integration, wearable photovoltaics and supply systems for low power electronics. For the development of flexible devices some critical issues still have to be solved, such as the use of solid or quasi-solid electrolytes and convenient sealing materials for the packaging, able to provide satisfactory duration in time.

This work presents the results obtained on a flexible DSSC, fabricated in our lab using UV-crosslinked polymeric membrane as electrolyte and titanium grids both as the anode and as the cathode substrate. The Ti grid was vertically dipped into a diluted (18NR-AO Active Opaque, Dyesol) TiO_2 paste, in order to obtain a suitable mesoporous semiconductive layer, which was subsequently annealed at 525 °C. The photoanode was then incubated into a 0.3 mM (Ruthenizer535bis-TBA, Solaronix) N719 dye solution for 15 h. The cathode was obtained depositing a 5 nm layer of platinum by means of sputtering [1]. Regarding the polymeric membrane, this was prepared UV-irradiating a solution of two oligomers (bisphenol A ethoxylate dimethacrylate, BEMA and poly(ethylene glycol) methyl ether methacrylate, PEGMA) and a free-radical photoinitiator [2]. The packaging was made with two 75-μm-thick PET foils and each layer of the cell was spaced by a thermoplastic foil. The sealing was performed using a hot press set at 85 °C.

Both rigid and flexible DSSC configurations have been tested by a careful characterization of their electrical performances. The small decrease in the overall efficiency of the flexible DSSC configuration with respect to the rigid one is related to the different quality of the electrodes/electrolyte interface contacts.

In conclusion, the simplicity of fabrication and the relatively low cost employed materials pave the way for an industrial scale-up and a possible future commercialization.

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FL-29

Actinoid vs Lanthanoid ions: the true story behind their similarity in water

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Actinoid ions, especially uranium and plutonium, are among the main components of nuclear wastes. This makes the knowledge of their hydration properties an important piece of information to improve the reprocessing procedures. For this reason, their structural similarities with the more "experimental friendly" lanthanoid ions is a topic of interest in coordination chemistry. Up to now, no direct proof of the exact correspondence between the actinoid and lanthanoid hydration complexes has been provided leaving it an open and debated question.

In this work, we have shed light into this issue by means of X-ray absorption near edge structure (XANES) spectroscopy that has been found to be the only experimental technique able to provide direct evidence of a one-on-one correspondence between the actinoid(III) and lanthanoid(III) ions in water. These results have been complemented by molecular dynamics simulations that provided a thorough picture (see Figure 1) of the hydration properties of actinoid ions in aqueous solution.

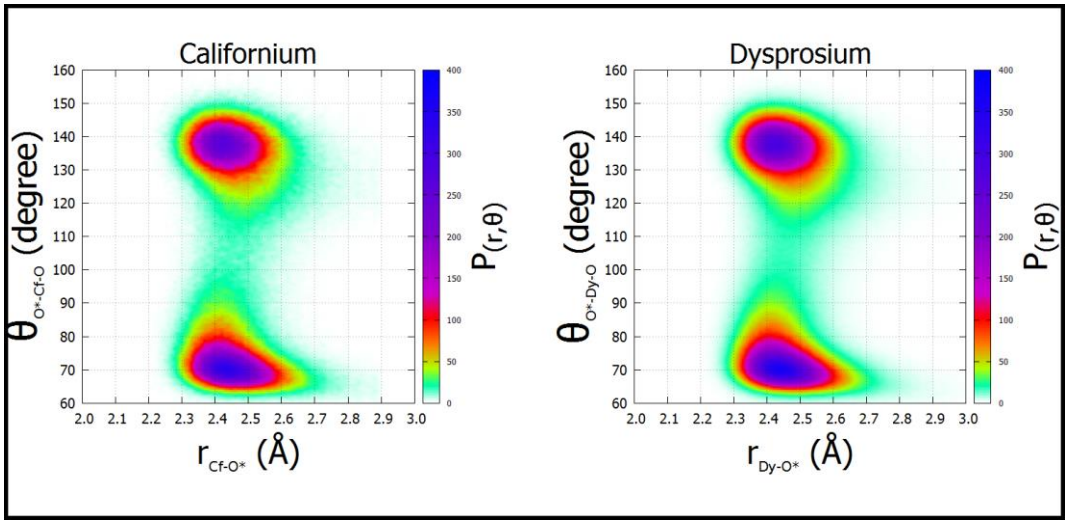

Figure 1: Distance-angle combined distribution functions for 9-fold hydration complexes of Cf(III) (left) and Dy(III) (right), showing an almost identical structure.

FL-30

Design and synthesis of thiazole-based polydentate ligands for the assembly of new metal-organic frameworks (MOFs)

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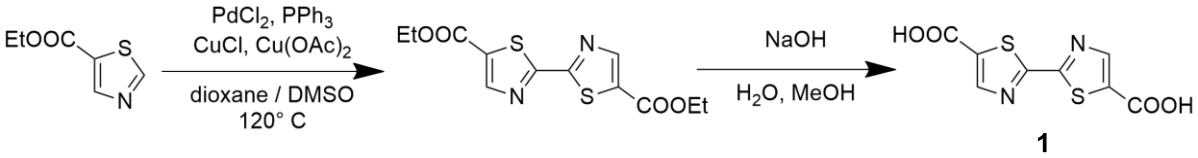
Metal–Organic Frameworks (MOFs) are porous materials built from metal-containing nodes and organic linkers. The virtually infinite combination of these two ingredients for the construction of MOFs is the key factor that makes them so successful for their practical exploitation in several fields of contemporary materials science [1].

Typical linkers are usually represented by polycarboxylic acids and polydentate N-heterocyclic bases (such as pyridines, imidazoles, pyrazoles and tetrazoles) [2]. There are fewer examples of spacers containing more than one heteroatom type in the heterocyclic core. The replacement of a carbon atom with a heteroatom (N, O, S) in the spacer structure modifies its electron density distribution. Heteroatoms may also be additional coordination sites for metal ions. Thiazoles are the simplest N,S-heterocycles [3].

The simultaneous presence of a hard (N) and a soft (S) base may favour the coordination to both hard and soft metal ions, making the related ligand more versatile for MOFs design. With this in mind, assorted ligands featured by both condensate (TzTz) and bonded (Tz-Tz, Scheme **1** and Figure **1**) thiazole rings have been synthesized and combined under solvothermal conditions with 3*d* metal salts to obtain MOFs. The results will be presented.



Scheme 1: Synthesis of the Tz-Tz ligand **1**.

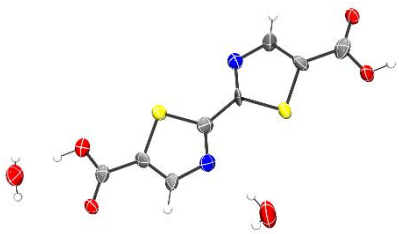


Figure 1: XRD structure of **1**· 2(H_2O).

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FL-31

Development and validation of an HPLC-FLD method for determination of 4'-geranyloxyferulic acid and its conjugate with L-NAME in mononuclear cells

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Oxyprenylated natural products represent a family of secondary metabolites that have been considered for years merely as biosynthetic intermediates of the most abundant C-prenylated derivatives. Many of the isolated oxyprenylated natural products were shown to exert in *vitro* and *vivo* remarkable anti-cancer and anti-inflammatory effects [1].

In the present study we developed a high-performance liquid chromatography with fluorescence detection method (HPLC-FLD) for the quantitative determination of 4'-geranyloxyferulic acid (GOFA) and its conjugate with the known *i*NOS inhibitor L-NAME (GOFA-L-NAME) (see Fig.1) in human mononuclear cells line cultures.

After extraction with methanol, GOFA and GOFA-L-NAME were separated on a reversed-phase column using a gradient elution program with water and methanol containing 1% of formic acid as the mobile phase. The proposed method was validated in terms of its linearity, sensitivity, accuracy (recovery) and precision (intra- and inter-day repeatability). The method was used successfully to evaluate for the first time the presence of these analytes in human mononuclear cells. Results showed that conjugate compound recorded higher intracellular accumulation than GOFA at different incubation times. Both samples reached the highest concentration after 4 h followed by a rapid decrease after 12 h.

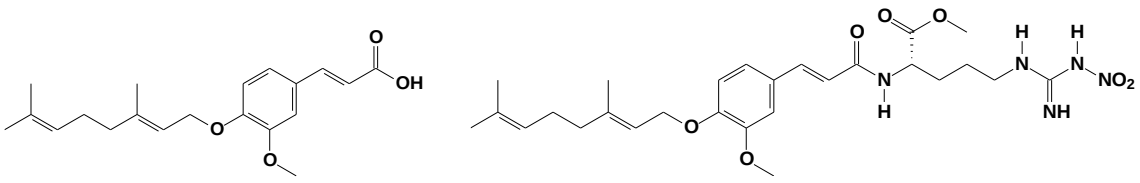

Figure 1. Chemical structures of GOFA and GOFA conjugate with L-NAME.

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FL-32

Cancer-related glycans recognition with benzoboroxoles for sensing technologies

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Compared to healthy cells, cancerous cells express glycoproteins with higher branched glycan structures and modified terminal carbohydrate moieties [1]. The recognition of cancer-related glycoproteins is therefore a highly attractive challenge. In this regard, benzoboroxoles are carbohydrate recognition receptors that can potentially meet such challenge through integration in sensing platforms to detect cancer related-glycans [2]. They show good ability to bind carbohydrates via the hydroxyl groups under physiological conditions. Particularly, they can bind carbohydrates in the pyranose form, which account for the large majority of biologically relevant oligosaccharides.

With this proviso in mind, this work investigates the formation and isolation of covalent complexes between suitable benzoboroxoles and prostate cancer-related glycans. These complexes are then capable to be used as templates for the molecular imprinting on gold surfaces, creating a pattern of binding sites able to accommodate the targeted glycans only (Figure 1) [3]. The affinity and selectivity of the imprinted surfaces are assessed by SPR analysis. This approach is expected to lead to the development of novel sensor platforms for the detection of glycoproteins, discriminating between healthy and cancerous glycoforms, thus providing a powerful diagnostic tool.

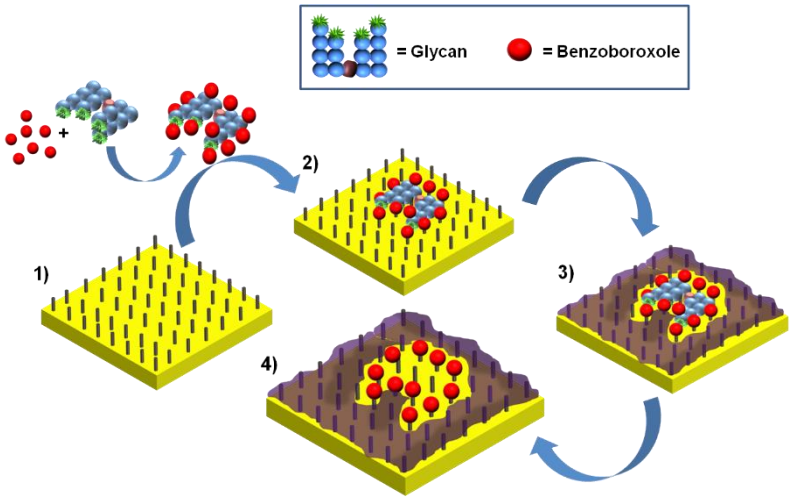

Figure 1: Fabrication of the imprinted gold surface.

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FL-33

Phosphoryl transfer processes promoted by a trifunctional calix[4]arene inspired by DNA topoisomerase I

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The appropriate functionalization of the upper rim of cone-calix[4]arene has been reported as an effective strategy for the creation of artificial catalysts able to cleave the phosphodiester function of nucleic acids and model compounds [1].

In order to mimic the catalytic triad at the active site of human DNA topoisomerase I6 [2], it was decided to synthesize the trifunctional calix[4]arene $(\mathbf{1}H_3)^{2+}$ [3], decorated at the upper rim with two guanidinium units and a phenolic hydroxyl group.

The catalyst, in its diprotonated form $(\mathbf{1}H_2)^{+}$, effectively promotes the cleavage of the DNA model compound bis(p-nitrophenyl) phosphate (BNPP) in 80% DMSO solution, showing a maximum activity at pH 9.5, where the rate enhancement of p-nitrophenol liberation relative to background hydrolysis was of 6.5×10^4-folds.

According to the experimental data the three active units cooperate during the reaction sequence in **Figure 1**, that involve a phosphoryl transfer process from BNPP to the nucleophilic phenolate moiety of the catalyst, followed by the liberation of a second equivalent of p-nitrophenol from the phosphorylated intermediate thanks to the electrophilic activation by the neighboring guanidine/guanidinium dyad.

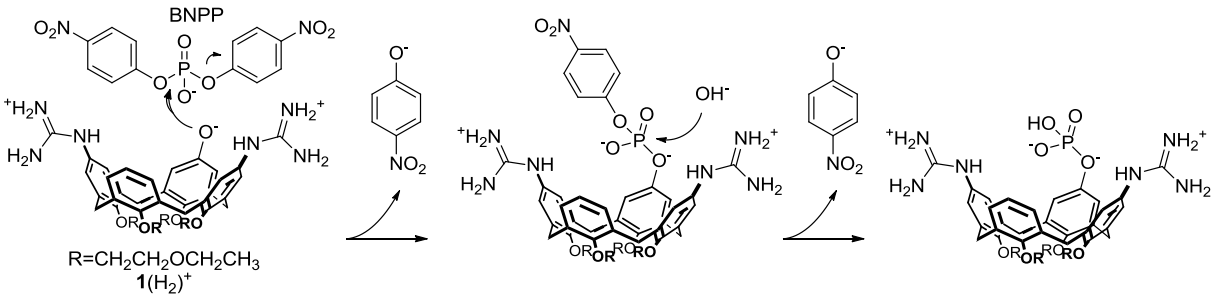

Figure 1: Proposed mechanism for the cleavage of BNPP by $(\mathbf{1}H_2)^{+}$.

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[2] M. R. Redinbo, L. Stewart, P. Kuhn, J. J. Champoux, and W. G. J. Hol, *Science* **279** (1998) 1504-1513.
[3] R. Salvio, S. Volpi, R. Cacciapaglia, F. Sansone, L. Mandolini and A. Casnati, *J. Org. Chem.*, DOI: 10.1021/acs.joc.6b01643.

Posters

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POS-1

Synthesis and anticancer activity of osmium complexes containing ethacrynic acid

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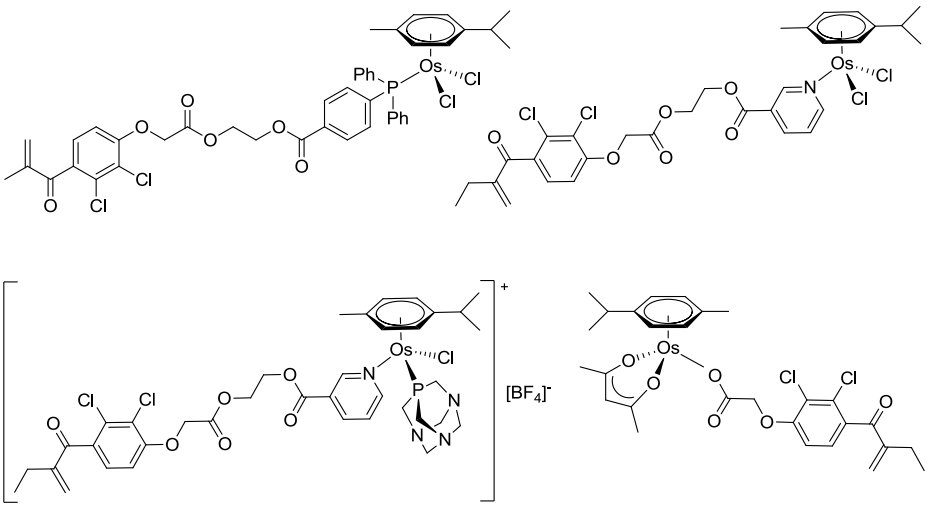
Exploiting the potentiality of bioactive organic compounds in the design of new organometallic drugs is a challenging field of research. In this context, ethacrynic acid (a potent inhibitor of glutathione S-transferases) is well-known for helping to overcome drug-resistance mechanisms [1]. Several Osmium complexes have proved to display anticancer activity [2]. The first Os (II) complexes containing the ethacrynic acid skeleton were synthesized either by direct coordination or via N- or P-donor ligands (see Scheme). The complexes were characterized by analytical and spectroscopic methods and by single-crystal X-Ray diffraction in two cases. Moreover, their stability in aqueous environment was elucidated by different techniques. The cytotoxicity of the new compounds was tested against human ovarian cancer cells and non tumorous human embryonic kidney cells. The inhibition of GST enzymes was ascertained through the evaluation of the residual GST activity after a period of incubation with the complexes and the ligands at IC_{50} concentrations.



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POS-2

New strategy for the dispersion of carbon filler in structural materials

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The use of carbon filler in the field of structural materials for engineering applications are currently highly considered, because offers the possibility to improve mechanical and electrical properties of the materials. However, this application show a real problem regards the dispersion of the nanofiller.

The innovation proposed consist in the use of a polymer bound to the filler that encourages a homogenous distribution of this in the materials and at the same time preserves the properties.

The new strategy allows to link a polymer on a carbon filler without modify a structure of the graphitic plane through non covalent interaction, in this way the property of the filler is preserved.

The synthesis of polymer involves a Ring Opening Metathesis Polymerization (ROMP) of a monomer by a Ruthenium catalyst. The carbene of Ruthenium is opportunely functionalized with a molecule of pyrene [1], so the polymer obtained have a terminal pyrene that is able, thanks at its aromatic system, to bind the polymer on the carbon filler via π-π stacking interaction.

Furthermore, the use of a pyrene allows also a better distribution of polymer in the filler, as evidenced by SEM images.

The polymer-pyrene than is dispersed in the carbon filler through simple stirring.

This strategy allow to link any polymer on any carbon filler.

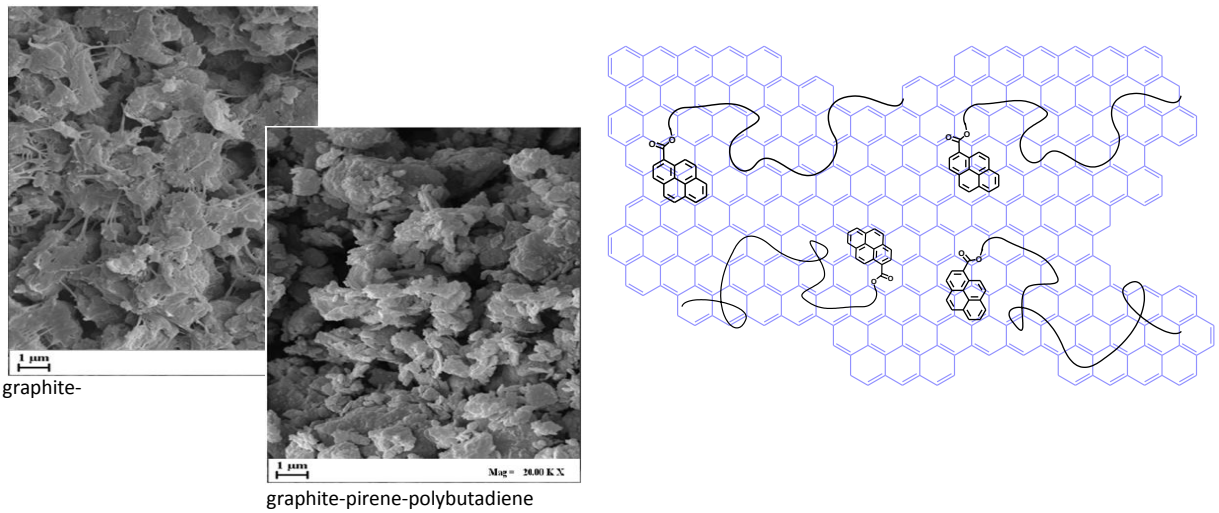

Figure 1: Images SEM of graphite-polybutadiene and graphite-pyrene-polybutadiene and schematic representation of π-π stacking interaction of pyrene-polymer on the graphitic plane.

[1] F. J. Gòmez, R. J. Chen, D. Wang, R. M. Waymounth and H. Dai, *Chem. Commun*. **2** (2003) 190-191.

POS-3

Unraveling the nature of the excited states of linear polyenes

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The present work rises in the framework of the *Orthogonal Valence Bond* (OVB) approach. The aim of this method is to combine in an efficient way the benefits of two of the main theories of modern Quantum Chemistry: the *Molecular Orbitals* (MO) and the *Valence Bond* (VB). It is well-known that the Molecular Orbitals theory is flexible and computationally very efficient and it allows for a compact description of the spectroscopic phenomena. On the other hand, the Valence Bond approach is much closer to the chemist way of thinking and, for instance, it makes possible to give an interpretation of the electronic wave function in terms of Lewis structures. Unfortunately, VB is computationally expensive, due to the non-orthogonality of its building blocks, and for this reason in the last decades it has not been widely used. The OVB method combines the computational efficiency of the MO approach and the conceptual benefits of VB. This is made possible by a Valence Bond reading of a correlated wave function obtained from the *Complete Active Space Self Consistent Field* (CASSCF) method, a well-known MO procedure.

The OVB approach allows one to analyze the wave function of the ground and excited states in local terms. In this study, the ground and excited states of the first terms of the series of the linear polyenes are considered following within this approach. Such a study is fundamental to understand the changes of the nature of the electronic distribution of the ground state upon excitation.

Figure 1 represents the most important electronic structures for the ground state of Hexatriene using OVB approach.

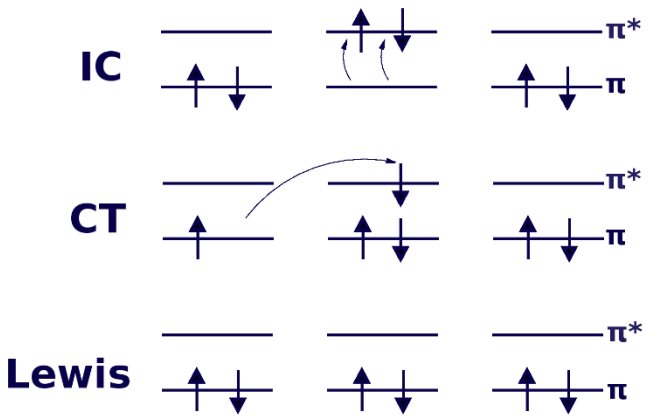

Figure 1: OVB electronic structures of hexatriene.

POS-4

Photocurable fluoropolymers improve efficiency and stability of perovskite solar cells

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Organometal halide perovskite solar cells have demonstrated high conversion efficiency but poor long term stability against ultraviolet irradiation and water. We show that rapid light-induced free-radical polymerization at ambient temperature produces multifunctional fluorinated photopolymer coatings that confer luminescent and easy-cleaning features on the front-side of the devices, while concurrently forming a strongly hydrophobic barrier toward environmental moisture on the back contact side. The luminescent photopolymers re-emit ultraviolet light in the visible range, boosting perovskite solar cells efficiency to nearly 19% under standard illumination. Coated devices reproducibly retain their full functional performance during prolonged operation, even after a series of severe aging tests carried out for more than 6 months.

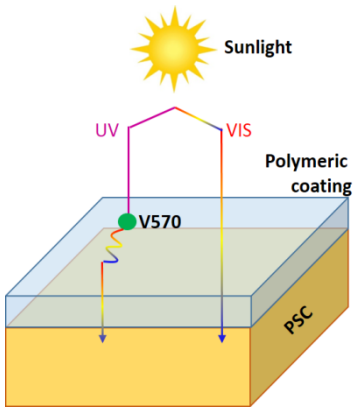

Figure 1: Scheme of the UV-coating operating principle.

[1] F. Bella, G. Griffini, J. P. Correa-Baena, G. Saracco, M. Grätzel, A. Hagfeldt, S. Turri and C. Gerbaldi, *Science*, DOI: 10.1126/science.aah4046.

POS-5

Solid-phase microextraction coupled to gas chromatography using hydrogen as carrier gas

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In this study we show how the use of solid-phase microextraction (SPME) technique coupled to a gas chromatograph (GC) equipped with flame ionization detector (FID), using hydrogen as carrier gas, can give hydrogenation reaction in the hot injector chamber. Preliminary results have been recently reported [1]. Considering that hydrogenation is a reaction carried out by molecular hydrogen, bringing to the addition of hydrogen to a double (or triple) bond, and it takes place at high temperature and high pressure, in presence of a catalyst, usually containing nickel, platinum, palladium or other metals, we have hypothesized that one or more components of the fiber can generate this phenomenon. In some cases, GC injector inserts containing an hydrogenation catalyst, have been specifically designed and applied to obtain an online hydrogenation, using hydrogen as carrier gas, in order to simplify the analysis of complex mixtures [2]. However, the use of SPME has never been reported to allow hydrogenation, when used with a normal GC injector insert for SPME. Several fiber assemblies, with different coatings and different cores, have been tested in this study. The extent of hydrogenation was determined by using a mixture of fatty acid methyl esters (FAMEs) from olive oil. The obtained results will be presented. Further studies are under investigation to assess also in quantitative terms the phenomenon for other unsaturated compounds and studying the influence of several parameters on this reactivity.

[1] D. Fiorini and M. C. Boarelli, *J. Chromatogr. A.* **1453** (2016) 134-137.
[2] S. M. Steinberg and D. W. Emerson, *Environ. Monit. Assess.* **184** (2012) 2119-2131.

POS-6

Removal of BTEX from water: super-expanded graphite as promising technology

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The longstanding and extensive use of crude oil and its derivatives represents one of the most extensive sources of environmental pollution. The gasoline leakage from storage tank or transportation pipelines, the incomplete oxidation of fossil fuels and the disposal of industrial effluents are the main ways to introduce hydrocarbon pollutants into the environment. Benzene, toluene, ethylbenzene and o-, m- and p- xylenes (BTEX) can be considered among the most dangerous components of the crude oil. Besides having a high content in crude oil (about 16 percent), BTEX mixture shows a high hazard potential related to its chemical-physical characteristics and its adverse health effects.

According to the Legislative Decree 152/2006 "Norms Concerning the Environment" of Italian Ministry of the Environment, the maximum permissible concentrations of benzene, toluene, ethylbenzene and xylenes in groundwater are 1 µg/l, 15 µg/l, 50 µg/l and 10 µg/l, respectively. These limits require the development and the use of specific treatments devoted to BTEX removal and their elimination from contaminated sites.

In recent years, among the most successful innovative technologies, absorption processes are certainly included. The research is now focused on new nanotechnologies and nanomaterials with best performances in terms of efficiency and environmental protection. Among them, graphene-based materials are giving encouraging results and are showing great potentials in the environmental field thanks to their peculiar features such as high specific surface area, exceptional electrical conductivity, electron mobility, excellent chemical and thermal stability.

In this study, we will investigate the adsorption capability of super-expanded graphite for water purification from a mixture of BTEX. In particular, we will focus on the massive adsorption and the ability to absorb BTEX from water to below maximum contaminant level regulated by Italian laws by graphene.

POS-7

Towards a comprehension of zinc oxide nanoparticles behavior in inorganic and biological fluids

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In recent years nanomedicine emerged as a preferred treatment option for many diseases. Zinc oxide nanoparticles (ZnO NPs) for their unique properties have received much attention for their implications in cancer therapy [1]. Recently, many efforts have been devoted to study ZnO NPs as diagnostic and therapeutic tools; however there is still a lack of knowledge about toxicity mechanisms and stability in the biological context. For clinical applications dispersed and stable nanoparticles are ideal and their aggregation behavior strongly depends on physico-chemical and surface properties.

In many studies ZnO NPs cytotoxicity is related to the production of Zn^{2+} ions [2], whose availability strongly depends on the extent of ZnO NPs dissolution and interaction with ionic species in solution.

In this scenario we decided to study ZnO NP stability in various solvents and biological media, focusing on NP aggregation and biodegradation. We synthesized ZnO NPs and characterized their morphological, chemical and physical properties [3]. In addition, we studied the stability behavior of ZnO NPs in different media, investigating parameters (particle concentrations, functionalization with aminopropyl groups and solvent nature) that would influence their hydrodynamic size, zeta potential and thus aggregation and degradation.

For this reason, we performed long term biodegradation analysis (up to one month) of these NPs in common cell culture media (EMEM) and in a simulated body fluid (SBF) mimicking human plasma. We demonstrated that our ZnO NPs aggregate rapidly when suspended in any media, independently from the synthetic batch. The rate of aggregation is however different depending on solution composition and ZnO concentration, reaching the maximum in SBF and EMEM. Long term biodegradation analysis showed that this aggregation is accompanied by small dissolution that does not affect the crystalline structure.

[1] E. Lim, T. Kim, S. Paik, S. Haam, Y. Huh and K. Lee, *Chem. Rev.* **115** (2015) 327-394.
[2] J. Liu, X. Feng, L. Wei, L. Chen, B. Song and L. Shao, *Crit. Rev. Toxicol.* **46** (2016) 348-384.
[3] V. Cauda, R. Gazia, S. Porro, S. Stassi, G. Canavese, I. Roppolo and A. Chiolerio, "Handbook of Nanomaterial Properties. XXVII", Springer Verlag, Berlin Heidelberg, 2014.

POS-8

Impurity profiling by capillary electrophoresis: definition of the design space within quality by design approach and investigation of separation mechanism and selectivity

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A Quality by Design (QbD) approach has been applied for the set-up of a capillary electrophoresis (CE) method for the simultaneous determination of the enantiomeric purity and of related substances of the chiral drug ambrisentan, an orphan drug used in the treatment of pulmonary arterial hypertension. QbD scouting made it possible to select cyclodextrin modified-micellar electrokinetic chromatography as operative mode, using sodium dodecyl sulphate (SDS) as surfactant for obtaining the micellar pseudostationary phase and γ-cyclodextrin (γ-CD) as chiral selector. This system involved complex separation mechanisms, including electrophoretic mobility, partitioning into the micelles and inclusion complexation into the cyclodextrin, and was essential for obtaining the separation of ambrisentan enantiomers and the other impurities. A first screening phase was followed by response surface methodology, which allowed the design space to be defined in combination with Monte-Carlo simulations. The built mathematical models represented a step forward in the comprehension of the electrophoretic behaviour of the analytes confirming the successful binomium of multivariate strategies and CE. Molecular Dynamics (MD) and NMR studies, essential tools for exploring the mechanism of molecular recognition, contributed to the understanding of the involved intermolecular interactions and to evaluate the mechanism of separation. MD simulations and NMR experiments underlined the ability of γ-CD of including SDS monomer forming inclusion complexes and the pivotal role of this surfactant in modulating the different affinities of the analytes for the chiral selector.

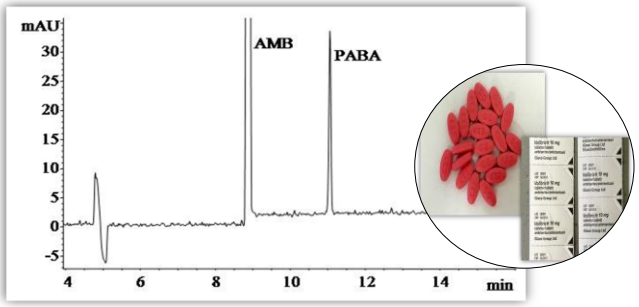

Figure 1: Electropherogram of a real sample of coated tablets of Volibris®.

POS-9

Structure and properties of new organic charge transfer complexes

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The discovery of the organic metal TTF-TCNQ (tetrathiafulvalene-tetracyano quinodimethane) in 1973 represented a milestone in research conducted on organic charge transfer complexes. Recently, attention has focused on their technologically-relevant properties, such as ambipolar transport, metallicity, photoconductivity, ferroelectricity or magnetoresistance wich led to the development of organic field-effect transistors (OFETs), organic photovoltaic cells (OPVs), and organic light emitting diodes (OLEDs). In binary charge transfer (CT) organic crystal one component acts as an electron donor (D) and the other as an acceptor (A). In these crystals there is a strong relationship between the crystal geometry and the electronic, optical and charge transport properties of the system. The choice of donor and acceptor and their organization within the CT crystal are likely the most important factors in determinating its electronic properties; indeed, the electronic coupling between the HOMO of the donor and the LUMO of the acceptor molecules yields a partial degree of charge transfer. One of the most interesting concepts related to donor and acceptor choice is the potential for band engineering. Several theoretical studies have shown that the donor HOMO will have larger contribution to the HOMO of the CT, whereas the CT LUMO correlates more to the acceptor LUMO [1].

In this work the structural and electronic properties of five newly synthesized TCNQ-containing CT complexes are studied and compared to get a better insight into their transport properties. As an example, in figure 1 the crystal structure and calculated orbitals for TCNQ-ferulic acid CT complex are shown.

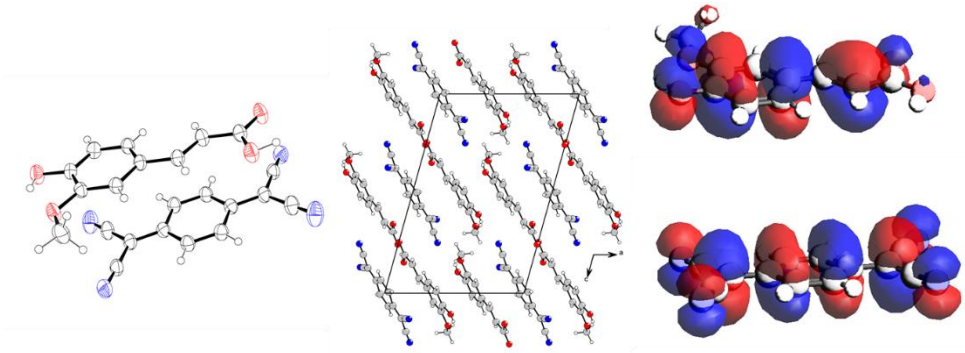

Figure 1: Crystal structure and HOMO and LUMO orbitals for TCNQ-ferulic acid complex.

[1] I. Shokaryev, A. J. C. Buurma, O. D. Jurchescu, M. A. Uijttewaal, G. A. De Wijs, T. T. Palstra and R. A. de Groot, *J. Phys. Chem. A.* **112** (2008) 2497-2502.

POS-10

Aminotriphenolate Co^{II}/Co^{III} complexes: synthesis, characterization and catalytic properties

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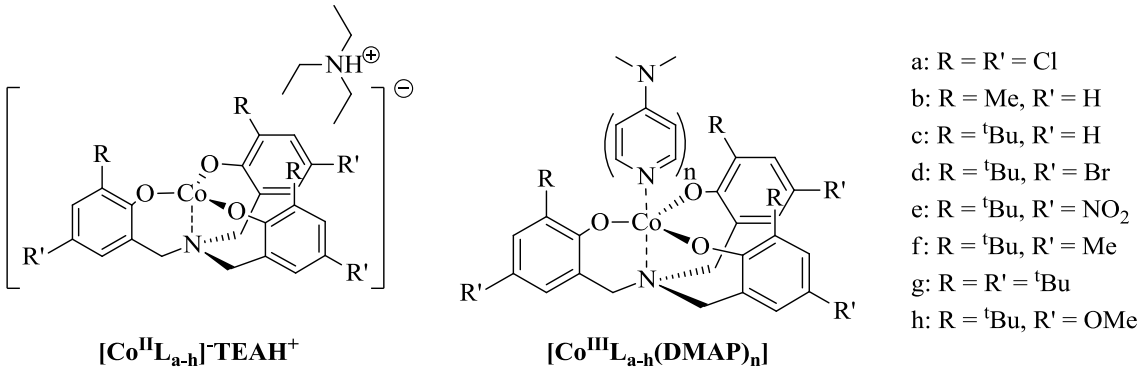
Cobalt complexes are becoming more attractive as cobalt is an earth-abundant, low-cost transition metal. Triphenolamines are a class of molecules whose structure is modular, and whose coordination chemistry with late first-row transition metals has been scarcely investigated [1,2]. In the present communication, we will report on the synthesis and characterization (FT-IR, UV-Vis, ESI-MS, MALDI-TOF-MS, NMR, CV) of aminotriphenolate Co^{II}/Co^{III} complexes (Figure 1).



$[Co^{II}L_{a-h}]^{-}TEAH^{+}$ $[Co^{III}L_{a-h}(DMAP)_n]$

Figure 1: Aminotriphenolate Co^{II}/Co^{III} complexes.

XRD structures have been obtained for three complexes [3]. In particular the XRD structure of $[Co^{III}L_a(DMAP)_2]$ shows an unprecedented ion pair Co^{II}/Co^{III} unit. Preliminary Cyclic Voltammetry tests showing activity in the catalytic Water Oxidation will be reported as well.

[1] C. Martìn, C. J. Whiteoak, E. Martin, E. C. Escudero-Adàn, J. R. Galàn-Mascaròs and A. W. Kleij, *Inorg. Chem.* **53** (2014) 11675-11681.
[2] M. Kaß, J. Hohenberger, M. Adelhardt, E. M. Zolnhofer, S. Mossin, F. W. Heinemann, J. Sutter, and K. Meyer, *Inorg. Chem.* **53** (2014) 2460-2470.

POS-11

Photoelectrochemical degradation of emerging contaminants in aqueous matrix at WO_3 interfaces

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The possibility of carrying out the photoelectrolytic water decontamination with WO_3 in diluted aqueous solutions with respect to both electrolyte and contaminant target concentrations has been carried out [1]. This application has relevance in the framework of the protection of water resources, of both fresh and salt water. In fact, the re-use of wastewaters will be necessarily an increasing practice especially in country with water scarcity. This practice, however, is not without drawbacks, bringing potential health risks due to the presence of highly toxic organic pollutants in wastewater. Among the contaminants, those of emerging concerns (CECs), which include pharmaceuticals, detergents and hormones, were proved to be only partially removed by conventional wastewater and recycled water treatments. Therefore, CECs remain in the treated waters where they may have adverse long-term impact on both human health and life of aquatic organisms.

In this contribution, we report on the photo-electrochemical degradation under UV and visible light of pharmaceuticals of emerging environmental concern. The ability of WO_3 supported thin films (photoelectrodes) to photodegrade the organic pollutants under consideration was tested and a considerable acceleration of the degradation kinetics (up to 4-5 times) was obtained through the application of a potential bias.

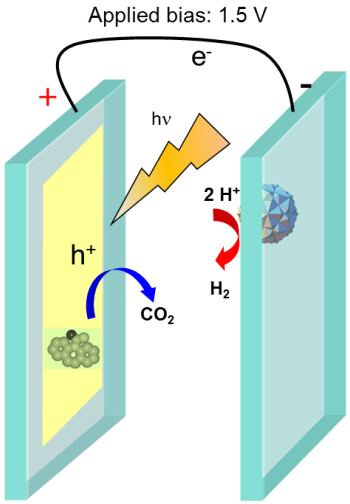

Figure 1: Scheme of photoelectrocatalytic experiments

[1] G. Longobucco, L. Pasti, A. Molinari, N. Marchetti, S. Caramori, V. Cristino and C. A. Bignozzi, submitted to *Appl. Catal., B.*

POS-12

In-depth mass spectrometric investigation of 1,8-DHN-based melanin prepared *via* enzyme-mediated oxidative polymerization

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The term "melanin" embraces a heterogeneous group of polymeric amorphous natural substances without a defined structure shared by animals, plants, bacteria and fungi which represent the key components of the pigmentary system of such organisms. In the last two decades, melanin and melanogenesis have attracted growing interest due to the unique structural, antioxidant, photoprotective and optoelectronic properties of melanin-based polymers [1]. Notwithstanding that chemistry of eumelanin subclass has been widely investigated [2], very few studies are present in the literature reporting on allomelanins, which is the most heterogeneous group of natural melanins of non-animal origin.

In the fungal kingdom, the black pigment of ascomyces fungi derives from oxidation and polymerization of the chromogen 1,8-dihydroxynaphthalene (1,8-DHN), producing 1,8-DHN-melanin-type, whose structure is still unrevealed [3].

Herein we report on the *in vitro* polymerization of 1,8-DHN under controlled biomimetic conditions, using two different oxidative systems, such as horseradish peroxidase/hydrogen peroxide and laccase/air. The structure of poly(1,8-DHN) has been deeply studied by Electrospray Ionization Mass Spectrometry (ESI MS) and Ultra Performance Liquid Chromatography (UPLC)-ESI MS analyses. Furthermore, the dimeric intermediate of the poly(1,8-DHN) has been successfully isolated and characterized by NMR spectroscopy, providing new insights on the mode of polymerization of such melanin precursor and allowing for a first structural hypothesis of 1,8-DHN-based melanin.

[1] M. D'Ischia, K. Wakamatsu, F. Cicoira, E. Di Mauro, J. C. Garcia-Borron, S. Commo, I. Galvàn, G. Ghanem, K. Kenzo, P. Meredith, A. Pezzella, C. Santato, T. Sarna, J. D. Simon, L. Zecca, F. A. Zucca, A. Napolitano and S. Ito, *Pigment Cell Melanoma Res*. **28** (2015) 520-544.
[2] S. Reale, M. Crucianelli, A. Pezzella, M. D'Ischia and F. De Angelis, *J. Mass. Spectrom*. **47** (2012) 49-53.
[3] M. J. Beltràn-Garcìa, F. M. Prado, M. S. Oliveira, D. Ortiz-Mendoza, A. C. Scalfo, A. Pessoa Jr., M. H. G. Medeiros, J. F. White and P. Di Mascio, *PLoS ONE* **9** (2014) e91616.

POS-13

NO photoreleaser-deoxyadenosine and -bile acid derivative bioconjugates as novel potential photochemotherapeutics

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This contribution reports the synthesis of some novel bioconjugates with anticancer activity and able to release nitric oxide (NO) under visible light excitation [1]. The 4-nitro-2-(trifluoromethyl)aniline derivative, a suitable NO photodonor, was conjugated with 2′-deoxyadenosine and urso- and cheno-deoxycholic acid derivatives, through a thioalkylic chain or the 4-alkyl-1,2,3-triazole moiety [2]. Photochemical experiments demonstrated the effective release of NO from 2′-deoxyadenosine and ursodeoxycholic acid conjugates under the exclusive control of visible light inputs [3]. Studies for the *in vitro* antiproliferative activity against leukemic K562 and colon carcinoma HCT116 cell lines are reported for all the compounds as well as a case study of photocytotoxicity against HCT116.

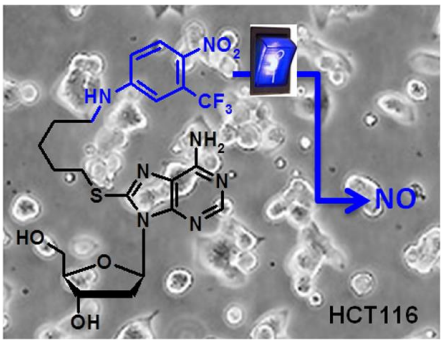

Figure 1: The synthetized NO photoreleaser-deoxyadenosine bioconjugate.

[1] D. A. Riccio and M. H. Schoenfisch, *Chem. Soc. Rev.* **41** (2012) 3731-3741.
[2] D. Perrone, O. Bortolini, M. Fogagnolo, E. Marchesi, L. Mari, C. Massarenti, M. L. Navacchia, F. Sforza, K. Varani and M. L. Capobianco, *New J. Chem.* **37** (2013) 3559-3567.
[3] P. N. Coneski and M. H. Schoenfisch, *Chem. Soc. Rev.* **41** (2012) 3753-3758.

POS-14

Design and synthesis of 3-phenylquinolone derivatives as nontuberculous mycobacteria efflux pumps inhibitors

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Giuseppe Manfroni, Stefano Sabatini, and Violetta Cecchetti

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Although *M. tuberculosis* is the most known, the incidence of Non-tuberculous mycobacteria (NTM) infections is by now a serious harm for the public health [1]. Among all the NTM pathogens, *M. avium* and *M. intracellulare* (grouped together in *Mycobacterium Avium Complex* - MAC) are the most frequent etiologic agents of pulmonary diseases caused by NTM. Treatment for MAC infections consists of a macrolide antibacterial during at least one year, but drug resistance associated to efflux pump (EP) activity develops easily during therapy. Therefore, the use of EP inhibitors (EPIs) could be a successful strategy to restore the activity of the extruded antibiotics.

Previously, we showed that NorA EPIs (NorA is the most expressed efflux pump in *S. aureus*) also exhibit an excellent EPI activity against MAV_1406, an efflux pump of *M. avium* [2]. Taking advantage from our experience in the field of *S. aureus* EPIs, with the aim to obtain a new series of *M. avium* EPIs, in this work we have designed and synthesized a series of 3-phenylquinolone derivatives (Figure 1) by merging the structures of 2-phenilquinoline NorA EPIs [3] and biochanin-A, a known EPI of *M. smegmatis*. Among them, two compounds showed a very promising EPI activity together with an good safety profile.

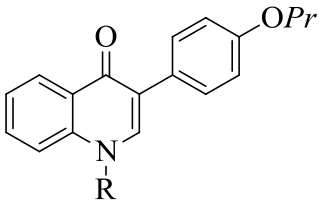

Figure 1: General structure of the 3-phenylquinolone EPIs.

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[2] D. Machado, R. Cannalire, S. S. Costa, G. Manfroni, O. Tabarrini, V. Cecchetti, I. Couto, M. Viveiros and S. Sabatini, *ACS Infect. Dis.* **1** (2015) 593-603.
[3] S. Sabatini, F. Gosetto, N. Iraci, M. L. Barreca, S. Massari, L. Sancineto, G. Manfroni, O. Tabarrini, M. Dimovska, G. W. Kaatz and V. Cecchetti *J. Med. Chem.* **56** (2013) 4975-4989.

POS-15

Design and synthesis of new cannabinoid receptor ligands

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Endocannabinoids are lipidic mediators, which include amides, esters and ethers of long-chain polyunsaturated fatty acids, and active specific membrane receptors, such as CB_1, mainly localized in the central nervous system (CNS), and CB_2, predominantly present in the periphery. The therapeutic use of CB_1 agonists is limited by side effects in the CNS, which can be restrict by increasing CB_2 receptor selectivity with ligands potential able to exert desired effects, such as those analgesic and antinflammatory [1].

Two series of 3-aroyl-2,5-dimethylpyrrole derivatives with a good affinity for the CB_1 and CB_2 receptors behaved as agonists, partial agonists or antagonists were previously studied by us and structure-activity relationships (SARs) were carried out [2,3].

Therefore, with the aim of extending the SARs and to obtain selective ligands we designed and synthesized new 1-alkyl-2,5-dimethyl-3-ketopyrrole substituted analogues. In particular, we considered that the variation of alkyl groups in the 1-position of the heterocycle could increase the affinity and selectivity towards CB receptors, and that the arylalkyl group on the 3-position could allow to get information on electronic characteristics, planarity and steric hindrance. Globally, our optimization process was led by modification on the pyrrole nucleus to hinder penetration of the blood brain barrier and favor *per os* administration, that could be achieved by improving the value of topological polar surface area and decreasing the value of clogP.

By preliminar *in vitro* tests it appears that some compounds can be considered as selective ligands of the CB_2 receptors.

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[2] G. Tarzia, A. Duranti, A. Tontini, G. Spadoni, M. Mor, S. Rivara, P. V. Plazzi, S. Kathuria and D. Piomelli *Bioorg. Med. Chem.* **11** (2003) 3965-3973.
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POS-16

CO_2 fixation in cyclic carbonates by salalen aluminum complexes

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The use of carbon dioxide as a renewable raw reagent for the production of materials is a topic of high interest. CO_2 is a highly abundant, inexpensive and non-toxic one-carbon source. The drawback is its high stability that leads to low reactivity. To overcome this issue, reactions with highly energetic molecules have been taken into consideration. In particular, the transformation of epoxides and carbon dioxide into either cyclic carbonates or aliphatic polycarbonates is of commercial importance [1]. There are a lot of applications associated with cyclic carbonates, such as their use as electrolytes in lithium ion batteries, polar aprotic solvents and intermediates in organic synthesis [2]. Among the catalytic systems developed for the synthesis of cyclic carbonate from epoxides and CO_2, a special attention has been devoted to catalysts deriving from inexpensive, earth-crust abundant metals, such as aluminum [3]. In this contribution, we report the synthesis and characterization of aluminum complexes (see figure 1) bearing salalen ligands (hybrid structures between salen and salan ligands). These complexes have been employed as catalysts for CO_2/epoxide cycloaddition reactions and resulted active with both terminal and internal epoxides, even working under mild conditions (low CO_2 pressure and low catalyst loading). NMR mechanistic studies have been carried out to shed light on the catalytic cycle active with this class of catalysts.

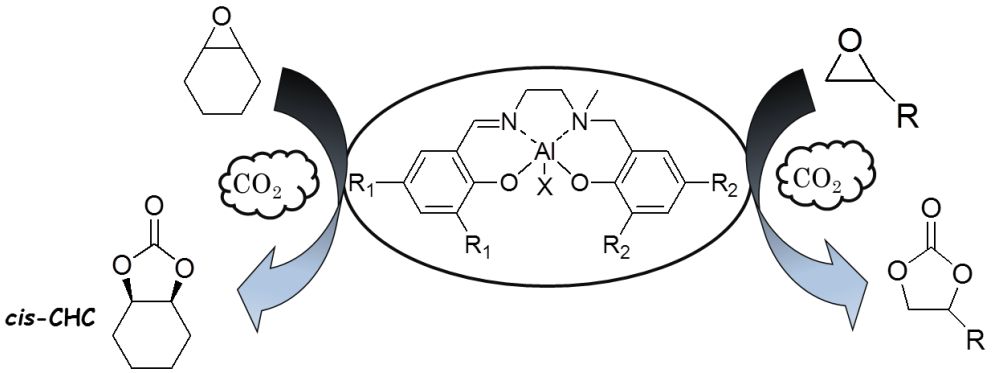

Figure 1: Aluminum complexes as catalysts for CO_2/epoxide reactions.

[1] M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.* **114** (2014) 1709-1742
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POS-17

Preparation of 1,2-propanediol through glycidol hydrogenolysis

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Nowadays, the development of a green and sustainable chemical industry for the production of bio-based feedstocks has attracted an increasing interest. One of the major investigated field is focused on glycerol and its conversion in value-added products [1]. The conversion of glycerol to epichlorohydrin (ECH) represents a consolidated industrial process developed in 2011 by Solvay, the so called Epicerol process. Herein, glycerol is converted into epichlorohydrin (ECH), the main monomer for the production of the epoxy resins, with an estimated global market of 2.2 Mt in 2020. Recently, we have proposed an innovative synthetic pathway to produce glycidol (2,3-epoxy-1-propanol) through a new and highly efficient route based on the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant [2].

Here we report on the synthesis of 1,2-propanediol (propylene glycol) through catalytic hydrogenolysis of glycidol, obtained as value-added product from the epichlorohydrin production plant, over Pd/C catalyst [3]. We also show the prominent effect of the acidic resin Amberlyst-15 in the selective and quantitative conversion of glycidol. Under the investigated reaction conditions, 1,2-PD is obtained with high yields and selectivity (>99%) in only 1 h under mild reaction conditions (80°C and 8 bar of H_2).

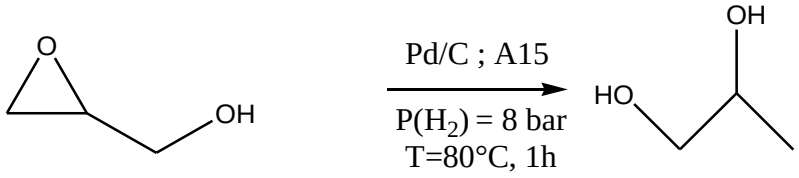

Figure 1: Reaction scheme for glycidol hydrogenolysis.

[1] D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chieregato, J. L. Dubois and F. Cavani, *Green Chem.* **17** (2015) 343-355.
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POS-18

Synthesis of linear guazatine derivatives as antibacterial agents

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Nowadays the antibiotic resistance is becoming a serious threat for the public healt, in fact it has reached alarming levels in many clinically-relevant human pathogens, both Gram-positive and Gram-negative bacteria [1].

Our research group has been involved for years into in-depth studies on derivatives of commercial guazatine, a mixture of polyamines and polyaminoalkylguanidines used in agriculture as fungicide. The main components and their synthetic derivatives showed broad-spectrum antifungal properties [2]. A quite large number of compounds bearing guanidine moieties have been reported in the literature as broadly active agents against microbial pathogens.

A series of guazatine linear derivatives were synthesized and the antibacterial activity was evaluated with a panel of different bacteria, both Gram-positive and Gram-negative ones and clinical isolates, in particular the multi-drug resistant strains, showing a promising potent and broad-spectrum antibacterial activity. The *hit compound* has got a good *in vitro* profile that suggests us an innovative mode of action, perhaps specific [3].

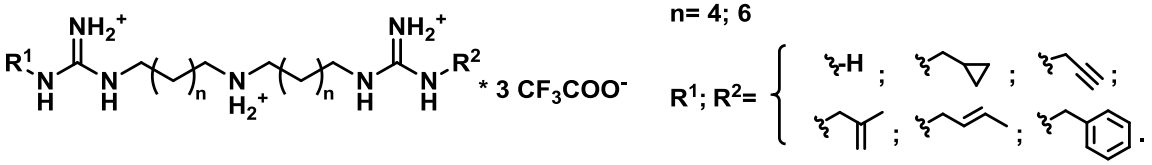

Figure 1: General structure of linear polyaminoalkylguanidine synthesized.

[1] B. Frazee, J. Lynn, E. D. Charlebois, L. Lambert, D. Lowery and F. Perdreau-Remington, *Ann. Emerg. Med.* **45** (2005) 311-320.

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POS-19

Graphenit-OX®@Cu as catalyst for batch and flow synthesis of substituted 1,2,3-triazoles

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Five-membered heterocycle containing three nitrogen atoms -triazole- is an interesting motif because of its presence in several bioactive molecules. The click chemistry reaction as the azide-alkyne cicloaddition (CuAAC) allows a highly regioselective synthesis of 1,2,3-triazoles. A sustainable copper catalysed flow process for CuAAC has been recently developed by Kappe [1]. Bodgan and Sach reported CuAAc reactions in a continuous Cu-coil flow reactor [2]. In this communication, we report the preparation and use in CuAAC of Cu_2O nanoparticles loaded on a Graphenit-OX®@Cu surface (7% Cu/graphenit-OX®@Cu). This research was aimed at investigating the catalyst's activity and recyclability in click chemistry reactions using the flow technology. The so developed Cu/Graphenit-OX®@Cu material was found to be effective either in batch or flow conditions and could be recycled. In addition, we investigated the Cu-leaching from the graphene surface by GFAAS analysis.

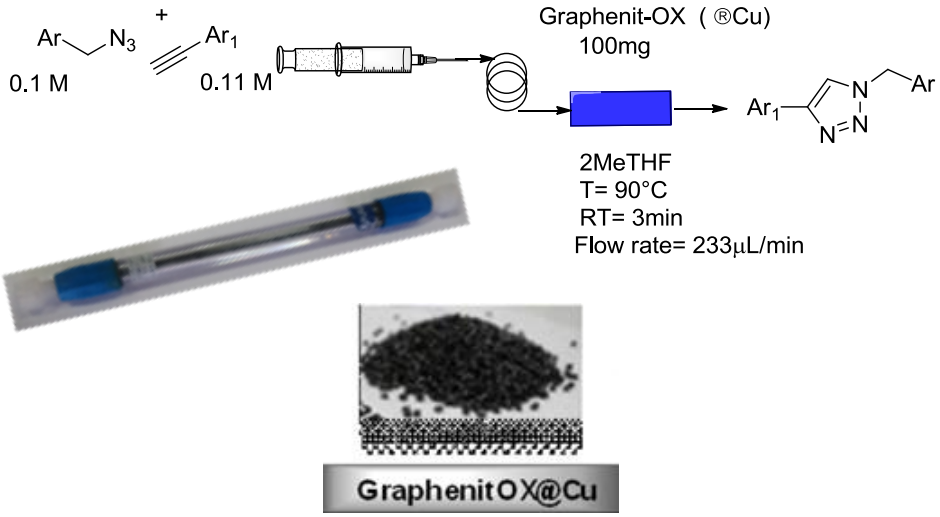

Figure 1: Flow synthesis

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POS-20

Synthesis of a basket-resorc[4]arene via metathesis reaction and encapsulation studies of fullerenes C_{60} and C_{70}

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Tetramerization of (*E*)-2,4-dimethoxycinnamic acid ω-undecenyl ester with ethereal BF_3 gave three resorc[4]arene stereoisomers which were assigned a *chair*, *cone*, and *1,2-alternate* conformation. The *cone* stereoisomer **1a** (Fig. 1) was submitted to olefin metathesis [1], using the second-generation Grubbs complex [$(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh)] as the catalyst, yielding resorc[4]arene derivative **2a** endowed with a large solvophobic basket-like cavity defined by two C_{20} hydrocarbon chain loops.

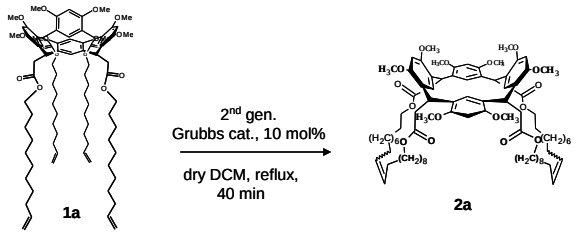

Figure 1: Olefin metathesis reaction on undecenyl resorc[4]arene **1a**.

Here we present an exhaustive study aimed at investigating the type of supramolecular recognition between resorc[4]arene **2a** and fullerenes **C_{60}** and **C_{70}**. Molecular modeling studies (namely, Docking [2] and Molecular Dynamics) showed that **2a** is able to efficiently encapsulate the fullerenes (Fig. 2). Therefore, encapsulation studies were carried out by UV spectroscopy and the equilibrium constants of the relative complexes were determined, providing a satisfactory agreement with molecular modeling data.

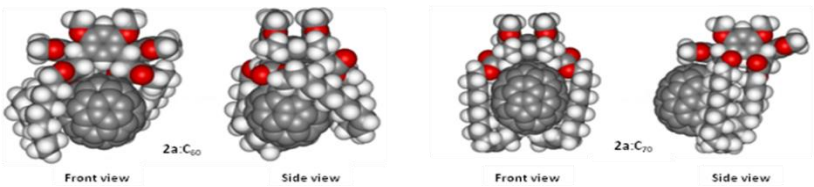

Figure 2: Computed structures of **2a:C_{60}** (left) and **2a:C_{70}** (right) complexes.

[1] (a) Y. Chauvin, *Angew. Chem. Int. Ed.* **45** (2006) 3740-3747; (b) R. R. Schrock, *Angew. Chem. Int. Ed.* **45** (2006) 3748-3759; (c) R. H. Grubbs, *Angew. Chem. Int. Ed.* **45** (2006) 3760-3765.

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POS-21

Sequential oxidative cyclizations of unprotected 2-alkynylanilines to anthranils

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Despite the relevance of N-O bonds in biologically active heterocycles, methods involving direct N-O bond formation to build up the oxazole nucleus are quite rare. Recently, we described an efficient approach to the synthesis of 2,1-benzisoxazoles through the oxidation of 2-aminoacylbenzenes with Oxone which achieved the direct N-O bond formation of the target heterocycle derivatives [1]. Moreover, as part of our ongoing interest in the synthesis of heterocyclic scaffolds based on atom-economical methodologies and easily accessible starting materials, we reported preliminary results on the development of a divergent sequential cyclization reaction of 2-alkynylanilines involving N-O/C-O bond formation leading to benzisoxazole derivatives by a suitable choice of the catalyst and reaction conditions.

We have developed an unprecedented Silver-catalyzed domino oxidative cyclization reaction of unprotected 2-alkynylanilines, leading to anthranils in moderate to good yields [2]. Full details of the results we have obtained as well as the study of the scope and limitations of this oxidative cyclization reaction will be shown.

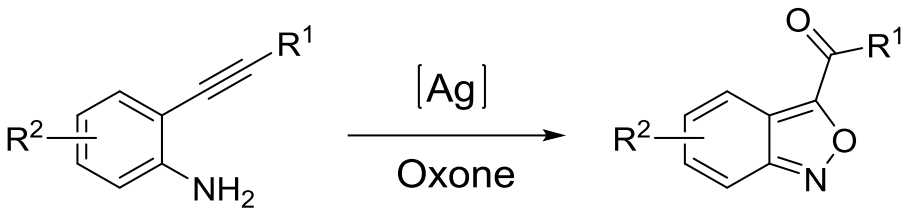

Figure 1: Sequential oxidative cyclization of unprotected 2-alkynylanilines.

[1] M. Chiarini, L. Del Vecchio, F. Marinelli, L. Rossi and A. Arcadi, *Synthesis* **48** (2016) 3017-3030.
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POS-22

Structural evidences and mechanistic insights into the iron processing by M-type and H-type ferritins

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Twentyfour-mer Ferritins are ubiquitous iron-biomineralizing nanocage proteins, that concentrate thousands of iron(III) ions as a solid mineral.

The ferritin molecule is a multimeric system forming an external cage around the storage cavity. Iron(II) enters the protein shell through ion channels, and then along each subunit parallel to the cavity, reaches the active site where it is oxidized by O_2 and eventually enters the cavity [1].

Studying iron in ferritins is difficult because the protein provides only weak interactions to iron, which moves without resting at any tight binding site; the transient nature of protein-iron interactions translates into undetectable iron binding in the crystals.

A soaking/flash freezing method has been developed to allow aerobic and anaerobic addition of iron(II) to bullfrog [2] and human ferritin crystals [3]. Multi-wavelength anomalous diffraction data have been exploited to unambiguously detect the iron atoms in ferritin crystals. The method has allowed us to observe for the first time the iron binding sites to a vertebrate ferritin and to see how they evolve with time. The structural data, together with stop-flow kinetic data, provide new information about the mechanism for iron processing by ferritins.

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[2] C. Pozzi, F. Di Pisa, C. Bernacchioni, S. Ciambellotti, P. Turano and S. Mangani, *Acta Crystallogr. D Biol. Crystallogr*. **71** (2015) 1909-1920.
[3] C. Pozzi, F. Di Pisa, D. Lalli, C. Rosa, E. C. Theil, P. Turano and S. Mangani, *Acta. Crystallogr. D Biol. Crystallogr.* **71** (2015) 941-953.

POS-23

Switchable reactivity and dual purpose molecules: oxazolinylazetidine as a case study

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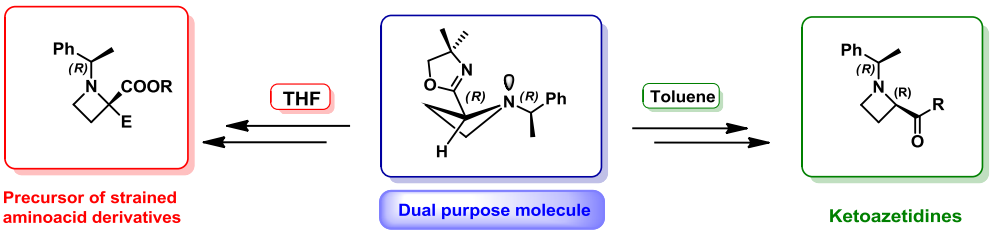
Our recent interest in the chemistry of four-membered heterocycles led us to disclose the importance of dynamic and complexation phenomena on the reactivity of such heterocycles [1]. In this communication we report results on the reactivity of chiral non-racemic oxazolinyl azetidines. Diastereomeric oxazolinylazetidines (*R*,*R*)-(*R*,*S*)- have been regioselectively lithiated at the α-position with respect to the oxazolinyl ring. The resulting azetidinyllithium compounds proved to be chemically stable but configurationally unstable in contrast to the corresponding α-lithiated oxazolinyloxiaziridines [2]. The (R,R) isomer, thermodynamically favoured, has been trapped with several electrophiles, furnishing chiral 2,2-disubstituted azetidines with high yields and high entantiomeric excesses at the lithiated C. It is noteworthy that with appropriate electrophiles, this is an easy and straightforward synthesis of precursors of strained aminoacid derivatives. Experimental evidences proved a solvent-dependent reactivity. Whereas the stereoselective lithiation occurs in α -position in coordinating solvents, such as THF, in Toluene the complexation between the lithiating agent and the oxazolinyl ring causes the addition to the oxazoline C=N bond, thus ending up with the formation of oxazolidines, which are precursors of useful chiral ketoazetidine, important synthons and building blocks in medicinal chemistry.



[1] M. Zenzola, L. Degennaro, P. Trinchera, L. Carroccia, A. Giovine, G. Romanazzi, P. Mastrorilli, R. Rizzi, L. Pisano and R. Luisi, *Chem. Eur. J.* **38** (2014) 12190-12200; G. Parisi, E. Capitanelli, A. Pierro, G. Romanazzi, G. J. Clarkson, L. Degennaro and R. Luisi, *Chem. Comm.* **51** (2015) 15588-15591; L. Degennaro, M. Zenzola, P. Trinchera, L. Carroccia, A. Giovine, G. Romanazzi, A. Falcicchio and R. Luisi, *Chem. Comm.* **5** (2014) 1698-1700; L. Degennaro, L. Pisano, G. Parisi, R. Mansueto, G. J. Clarkson, M. Shipman and R. Luisi, *J. Org. Chem.* **80** (2015) 6411-6418.
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POS-24

Compartmentalization of reagents into Pickering emulsions: divide et impera

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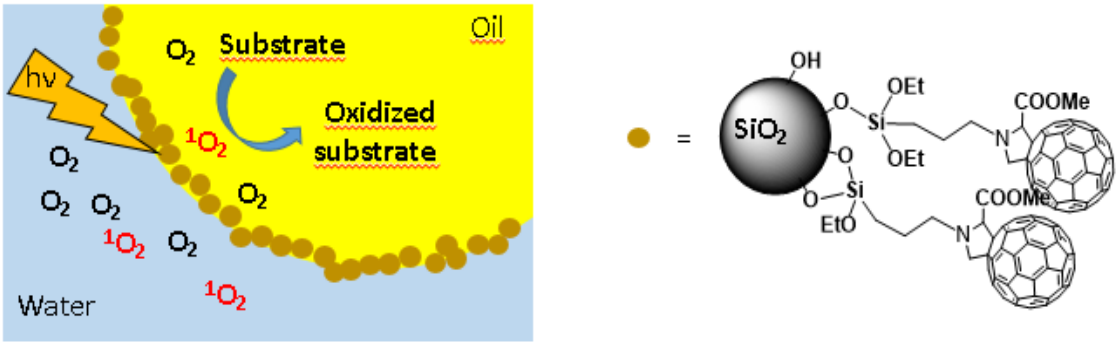
Organising nanoparticles in patterns is a challenging research endeavour towards the application of nanomaterials. Ordered structures answer homogeneously to external stimuli, such as pH, temperature and light [1], allowing a strict control on chemical and physical properties of the entire system. Pickering emulsions (emulsions stabilized by solid particles) provide a potential well at the water-oil interface that represents a strong driving force for the supra-colloidal assembly of nanoparticles [2].

Here is presented a proof-of-principle application of this concept, where functional silica nanoparticles capable of producing singlet oxygen upon light irradiation are organized over oil droplets as shown in the figure at the bottom. In this Pickering emulsion, each droplet effectively becomes a photocatalytic reactor that oxidizes a model compound dissolved in the organic phase by using oxygen molecules that diffuses from the atmosphere through water. The kinetic comparison between the performance of our droplet-microreactors and that of more traditional heterogeneous catalysis in the oil phase, showcases the potential of our approach.



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POS-25

Fenton reaction coupled to liquid chromatography with electrochemical detector for hydroxyl radical monitoring

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The most powerful free radical in biological systems is the hydroxyl radical (·OH), produced when hydrogen peroxide reacts with superoxide anion upon catalysis by a transition metal (iron or copper). This reaction is well known as "Fenton reaction".

The aim of this study is the development of an original analytical strategy to monitor ·OH formation via Fenton reaction by means of a liquid chromatographic system coupled to electrochemical detection (LC-ED). When salicylate is used as an indicator, ·OH production generates the following three phenolic products: 1,2-dihydroxybenzene, 2,5-dihydroxybenzoic acid and 2,3-dihydroxybenzoic acid. By performing kinetic tests, it was observed that ·OH production was linear with time up to 30 minutes, recording a satisfactory increase after 2 minutes from incubation.

Bioactive molecules can interact in different ways with mentioned metal ions in the reaction mixture: 1) inhibiting ·OH production by chelating activity and/or direct scavenging potential, 2) remaining inert, 3) reducing the transition metal and thus potentiating ·OH production.

For this purpose, some representative bioactive compounds were tested: quercetin, catechin, deferoxamine, trientine, ethylenediaminetetraacetic acid (EDTA), phloroglucinol, 3,4-dihydroxyphenylacetic acid (DOPAC), 3-hydroxyphenylacetic acid, homovanillic acid (HVA) and 5-chloro-7-iodo-8-hydroxyquinoline.

To evaluate the effect of bioactive molecules on ·OH generation, the three phenolic products were quantified and compared to Fenton standard reaction conditions.

Preliminary results are good, thus proving the suitability of this approach for studying the anti- or pro-oxidant activity of different substances. Further assays are in progress to complete method validation.

POS-26

Development of a liquid chromatography-tandem mass spectrometry method for the assessment of pharmacokinetics and metabolism of Berberine and Berberrubine in rat

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Berberine (BBR) is a natural tetraisoquinoline alkaloid mainly found in the plants of Berberis order. BBR is known since ancient times for its important beneficial properties, above all the lipid-lowering effect [1]. Scientific researches showed that this kind of activity is linked to the BBR capacity of increasing low-density lipoprotein receptor (LDLR) expression [2]. In order to explain BBR beneficial effects despite its low bioavailability, it has been proposed that the main biological activity must be correlated to its primary metabolites, which may represent the real *in vivo* active form. Among these metabolites, Berberrubine (M1) showed the highest up-regulatory effect on LDLR mRNA expression and the highest bioavailability [3]. Basing on these considerations, we assessed and compared pharmacokinetics and metabolism of M1 and BBR in a rat animal model. For this purpose, we developed and validated an HPLC-ES-MS/MS method for the quantitative determination of BBR, M1 and related metabolites in different biological matrices, such as blood, urines, liver, kidneys, intestinal contents and stools. Validation process was conducted in accord to ICH guidelines; good accuracy (bias%<10%) and precision (CV%<10%), very low detection and quantification limits (0.1–0.5 ng/mL) were obtained, ensuring sufficient sensitivity and selectivity for this kind of study. The optimized extraction procedures afforded recoveries higher than 90%, while matrix effects (M.E.) were negligible (M.E.%<15%). At the end of the study, 24 hours after administration, the total recovered dose of BBR and M1 was, respectively, 82% and 76%. Results showed a higher bioavailability of M1 after its direct administration respect to BBR, highlighting how M1 could be a potent and alternative phytotherapic compound for the treatment of dislipidemic diseases.

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POS-27

Electronic structure of substituted benzene: an OVB analysis

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The study of electronic structure of organic aromatic molecules is a very important topic in theoretical chemistry. To this aim, the wave function methods represent one the most powerful tools. The method we have used is called OVB (Orthogonal Valence Bond) and it combines the high precision of the Molecular Orbital (MO) methods with the local vision of the Valence Bond (VB) approaches. This allows one to get useful insights on the chemical nature of many molecules of interest. It is well-known that the MO theory is flexible and computationally efficient, and it allows a compact description of spectroscopic phenomena. On the other hand, the VB approach is much closer to the chemist way of thinking and, for instance, it makes possible to give an interpretation of the electronic wave function in terms of Lewis structures.

Starting from the *Complete Active Space Self Consistent Field* (CASSCF) wave function, in this work we compare a few aromatic organic molecules, say benzene and substituted benzene, and we describe the π electronic structures of these molecules in terms of building blocks presenting a clear distribution of the electrons over the Carbon atoms.

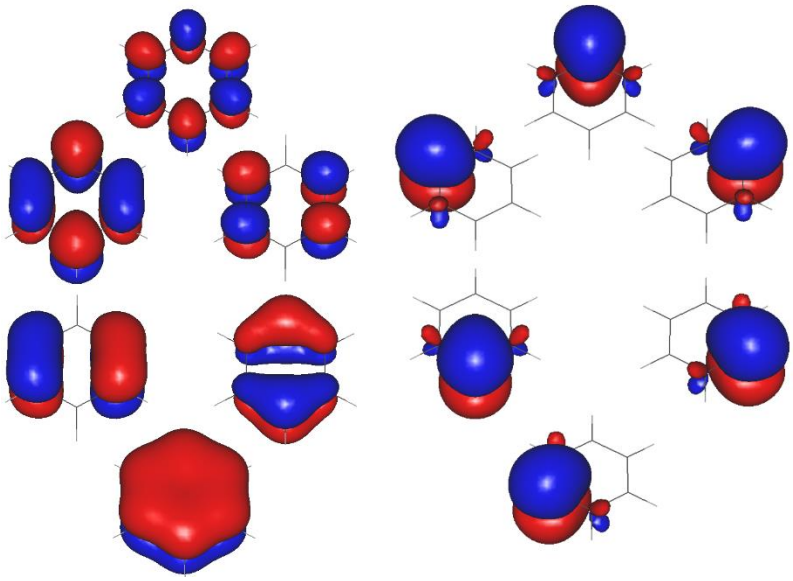

Figure 1: Benzene: Delocalized orbitals (left) and orthogonal atomic orbitals (right).

POS-28

Design and synthesis of conformationally restricted melatonin receptor ligands

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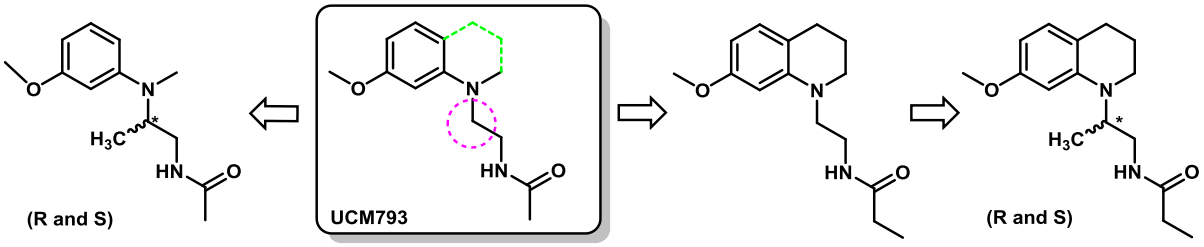
Melatonin (*N*-acetyl-5-methoxytryptamine, MLT) is a tryptophan-derived hormone primarily produced by the pineal gland and released into blood circulation during the darkness. Besides its primary role of regulating circadian rhythms, MLT is involved in a number of additional biological effects, many of which are mediated by the activation of GPCRs, named MT_1 and MT_2. We have recently developed a class of *N*-anilinoalkylamide derivatives that can be modulated to give compounds with different MT_1/MT_2 selectivity and intrinsic activity [1]. A derivative of this series, UCM793, has been used as pharmacological tool, to investigate melatonin receptor functions [2,3]. In order to obtain additional insight into structural parameters involved in the receptor binding, the development of UCM793 conformationally restricted analogues appears to be an interesting and rational approach.



Several derivatives were designed using different constraining strategies such as introduction of a β-methyl substituent on the ethylamido side chain, or the incorporation of *N*-CH_3 fragment into a tetrahydroquinoline ring. Synthetic approaches, stereochemistry and pharmacological studies of the new melatonin receptor ligands will be presented as well as a study on the relation between conformational and configurational aspects with the spatial arrangement of the amido side chain.

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POS-29

Aqueous electrolyte for DSSCs: DoE investigation on redox mediator and gelling agents

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Dye sensitized solar cells (DSSCs) are a promising and interesting technology able to convert solar light into electricity and have recently achieved efficiencies up to 14%. Nevertheless DSSCs are not yet commercialized on large scale due to their issues concerning safety and long-term stability. In fact, standard high-efficiency DSSCs are prepared mainly with organic solvent-based liquid electrolytes, *i.e.* acetonitrile and methoxypropionitrile, and are often characterized by high vapor pressure, toxicity and flammability.

In recent years, with the idea of creating efficient, safe, and low-cost DSSCs, the research moved the attention towards alternative solvent-based electrolytes. Above all, DSSCs with water-based electrolytes look like one of the best solution providing reduced costs, non-flammability, better stability, and environmental compatibility [1]. Moreover, the possibility of gelling the liquid solvent into a polymeric matrix can reduce the electrolyte leakage outside the device, increasing the long-term stability.

In this contribution, the investigation on a series of iodine-based 100% aqueous electrolytes is presented. Thanks to our knowledge [2,3] and to a multivariate approach, useful to perform DoE (Design of Experiment) investigation, the effects on DSSCs performance of the change in redox mediator concentrations and in photoanode preparation are evaluated. Finally, the gelation of aqueous electrolytes with a bio-derived polymer is also studied as well as their interesting photovoltaic performances.

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POS-30

Solubilization capabilities of a green surfactant towards DNAPLs

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Trichloroethylene (TCE) is a chlorinated solvent that belongs to the class of dense non-aqueous phase liquids (DNAPLs), and it is an ubiquitous environmental pollutant. In the last years, several remediation strategies have been developed for the removal of TCE from groundwater, including pump & treat (P & T) adsorption processes and phytoremediation [1]. An improvement of P & T is the surfactant co-solvent flushing method; in this technique a mixture of chemicals and surfactants are generally employed to enhance the dissolution of DNAPLs and, consequently, increase the extraction yield.

In this work we test the performances of the surfactant Synperonic 91/5 (Syn 91/5) to improve the aqueous solubility of TCE; being an ethoxylated alcohol, Syn 91/5 is considered a low-impact and biodegradable "green" surfactant. The dissolution of TCE into water solutions at increasing [Syn 91/5], was investigated by means of UV-VIS technique, having the TCE a characteristic absorption wavelength at λ= 200 nm [2]. As clearly show in figure 1, Syn 91/5 allowed to increase up to 15 times the TCE aqueous solubility. In this work the dependence of TCE solubility from temperature was also evaluated.

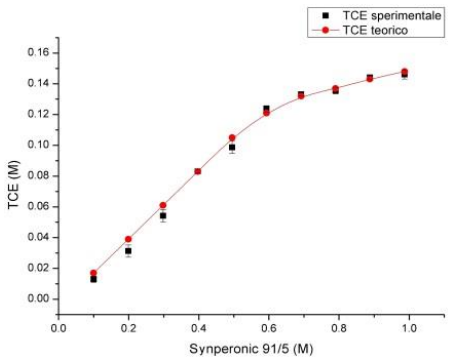

Figure 1: Dependence of TCE aqueous solubility from [Syn 91/5].

In conclusion, our results show that Syn 91/5 can improve the dissolution of TCE in water; This work encourage further studies for the employment of green surfactants in the surfactant co-solvent flushing technique.

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POS-31

Homo- and co-polymerization of epoxides and anhydrides promoted by bimetallic salen aluminum complexes: role of the cooperation between the two reactive metal centers

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Aliphatic polyesters are of great interest because of their good biodegradability and biocompatibility that make them suitable in pharmaceutical, biomedical and agricultural fields. They can be produced *via* Ring Opening Polymerization (ROP) of cyclic esters and Ring Opening Co-Polymerization (ROCOP) of epoxides and anhydrides. Although the polymer architecture obtained by ROP is limited, ROCOP is a promising opportunity to extend the range of the materials produced thanks to the diversity of functional monomers that are either commercially available or easily synthesized [1,2]. Both polymerizations occur though coordination-insertion mechanism promoted by metal complexes. While a plethora of catalysts is described for the ROP, a far narrower range is known for the ROCOP. In recent studies, dinuclear catalysts frequently showed superior performance compared to monometallic ones [2]. In this contribution, we report the action of a bimetallic salen aluminum complex and the related hemi-salen complex in the homo- and co-polymerization of epoxides with anhydrides. The bimetallic complex **1** revealed to be a powerful catalyst for the ROP of epoxides whereas the related hemi-salen complex **2** was inactive. The study highlights a synergistic action between the two metal centers of the dinuclear specie [3]. On the other hand, in the ROCOP both catalysts revealed high, and even more surprisingly, comparable activities suggesting that dinuclear cooperativity is not at stake.

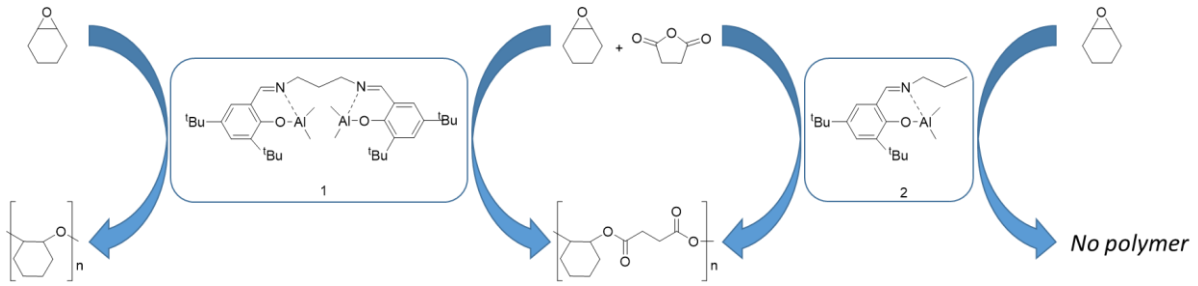

Figure 1: Role of the communication between the two reactive metal centers.

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POS-32

Dimeric Gd(III)-complexes as high field MRI contrast agents

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The key criteria to optimize the relaxivity of a Gd(III) contrast agent at high fields (defined as the region > 1.5 T) are relatively well understood [1] and can be summarized as follows: i) the occurrence of a rotational correlation time τ_R in the range of ca. 0.2 - 0.5 ns; ii) the rate of water exchange is not critical, but a τ_M < 200 ns is preferred; iii) a relevant contribution of the second sphere of hydration to the relaxivity. In addition, the use of macrocycle-based systems ensures the formation of thermodynamically and kinetically stable Gd(III) complexes.

The efficiency of a dimer depends primarily on the degree of flexibility of the linker, on the absence of local motions and the presence of contribution from the second sphere water molecules. The objective in this case is a relaxivity (for Gd) in the order of 10-15 $mM^{-1}s^{-1}$, especially if the two coordination cages are facing each other allowing the presence of a network of water molecules interacting via hydrogen bonds that can contribute greatly to the relaxivity [2].

Thus, two dimeric chelates derived from the well-known macrocyclic systems HPDO3A and DOTAMAP (Figure 1) were synthesized through a multistep synthesis. A complete ^1H and ^{17}O NMR relaxometric study was carried out in order to evaluate the parameters that govern the relaxivity associated with these complexes.

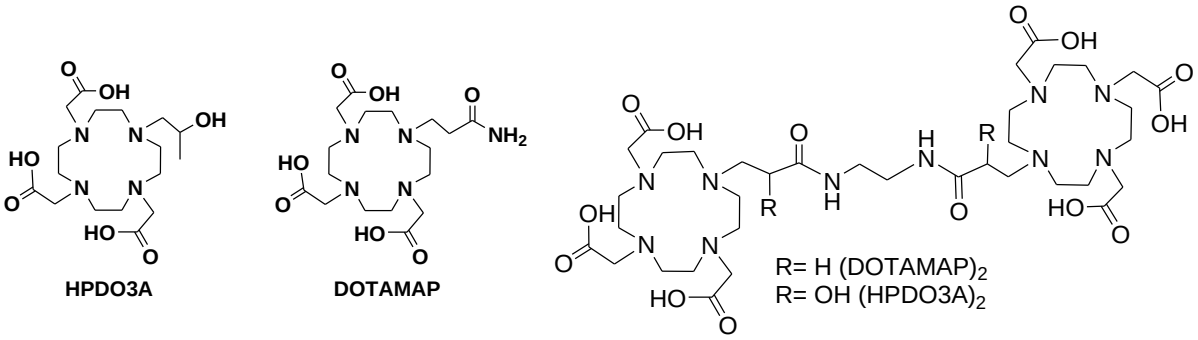

Figure 1: Monomeric and dimeric structures of DOTAMAP and HPDO3A

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POS-33

Ir(III)-ciclopentadienyl-pyridinyl-quinoline complexes: solution properties and polynucleotides binding

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There is an emerging interest in applying inorganic and organometallic transition metal complexes like new anticancer drug capable of interacting with DNA [1,2]. Recently, studies have focused on half-sandwich Ir(III) anticancer complexes, that can attack the DNA or perturbate the redox status of cells [3].

In this work we studied the interaction between the iridium complex shown in Figure 1 and biosubstrates as DNA, RNA and BSA. Firstly, the properties of the metal complex alone were analysed: the chloride exchange process (to give Ir-H_2O from Ir-Cl) and the acidity constants. Then, the possible binding reaction of the two species Ir-H_2O and Ir-OH^-, with biosubstrates was analysed through spectrophotometry, viscometry, circular dichroism and stopped-flow kinetics. The results obtained show some interesting interactions taking place, that will be discussed.

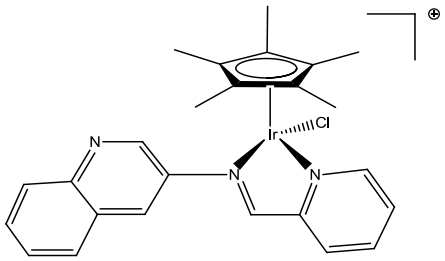

Figure 1: The metal complexes used in this study [Ir (η5-Cp*)Cl(quinpy)]Cl (quinpy = (E)-1-(pyridin-2-yl)-N-(quinolin-3-yl)methanimine).

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POS-34

SPR chemical sensors based on molecularly imprinted polymer in plastic optical fibers for food applications

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Fast and selective detection methods, for food control, are widely required. Sensor systems appear to be suited for such application, providing in addition good characteristics of small-size, low cost and easy and reproducible preparation, hence the possibility of designing a "Lab-on-a-chip" platform for "on-site" applications. Here, two different platforms for furfural detection in aqueous media are proposed. Furfural is widely present in food since is associated with toxic and carcinogenic effects. It is employed as a marker for the quality control of foods so its determination via sensors is particularly interesting. Both sensors, are based on molecularly imprinted polymer (MIP) synthetic receptor, which has some advantages over the bioreceptors, as for example antibodies, in terms of easy preparation, reproducibility, withstanding at working conditions different from classical biochemical environments (i.e. pH and temperature variation or matrix not biocompatible). The optical SPR-POF-MIP sensor is based on surface plasmon resonance (SPR) phenomena, where the shift in resonance wavelength is evaluated in function of the furfural concentration, [2]. The voltammetric SPC-MIP sensor, is based on square wave voltammetry (SWV) analysis, where the reduction current is evaluated in function of concentration [3]. The two platforms and their setups were obtained as previously described [2,3]. The optoelectronic sensor consists in a plastic optical fiber (POF) with a thin layer of Au in contact with the synthetic receptor (MIP). The electrochemical sensor is based on a commercially available screen printed cell, with graphite ink working and auxiliary electrodes, and a silver ink quasi-reference electrode. Both the sensors have very small dimensions (about 1 cm^2), and are suitable for measurements in small sample volumes. The results showed that the optical SPR-POF-MIP sensor is able to selectively detect the presence of furfural in aqueous media at concentration higher than $2.1*10^{-7}$M. The detection limit is similar to that previously demonstrated in mineral oil [2], sufficient for application in food controls. On the other hand SPC-MIP sensor shows a LOD of $6*10^{-6}$M which is almost one magnitude order higher than that obtained for SPR-POF-MIP. This LOD clearly needs to be improved for food applications, for example by modifying the sensing surface to enhance the conductivity and lower the capacity current.

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POS-35

Elemental analysis of metallic samples by nanoparticles-enhanced laser-ablation ICP-MS

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This conventional method of Solid sample analysis is very dirty and produces a lot of chemical waste. Conversely, laser ablation is a green technology because it does not require acid dissolution and does not generate chemical wastes.

Moreover, LA-ICPMS technique presents other interesting features such as high spatial resolution, extended linear dynamic range, low detection limits, extremely small sample quantities required for analysis.

We propose an analytical strategy to enhance the sensitivity of LA- ICPMS by the deposition of gold nanoparticles (AuNPs) on the surface of investigated samples. The undoubted strengths of this approach are represented by simplicity, low-cost budget and fast performance. The commercial LA-ICPMS set-up has not been changed in any way and laser parameters, type and flow of gas carrier is not modified to improve the ablation of the sample [1].

The sample surfaces have been altered by depositing metallic nanoparticle (NPs) colloidal dispersions, thus increasing their response to laser, but preserving their chemical properties. A consistent lowering of the breakdown threshold and a remarkable increase in the measured signal intensity have been observed. This has allowed to determine traces and ultratraces in many areas (environmental, forensic, clinical, cultural heritage, food analysis, ecc.).

In the method developed, the drops of NPs can be put in a controlled manner on the sample surfaces and completely removed before the analysis by laser ablation. This represents a further advantage compared to the classical methods of sample analysis.

The first results obtained with this technique in the analysis of metal matrices show enhancement of the signal of one order of magnitude for most of the analyzed metals.

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POS-36

BODIPY as photosensitizers in photodynamic therapy. A theoretical investigation

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Despite the research is making several headways, the cancer remains the major cause of death in the world. Alongside the traditional techniques, the photodynamic therapy (PDT) has emerged as noninvasive therapeutic option in the management of cancer and other diseases. PDT employs a PS able to transfer energy received from a light source to the oxygen present in tissues, generating reactive oxygen species (ROS) that attack key structural entities within the targeted cells, ultimately resulting in necrosis or apoptosis. To generate the highly cytotoxic singlet oxygen $^1O_2$ agent, a good photosensitizer must possess: (i) a red-shifted electronic absorption band falling in the so-called therapeutic window (600-800 nm), to penetrate human tissues allowing the treatment of deeper tumors; (ii) a high intersystem spin crossing probability between the excited S_1 and the T_1 electronic states; (iii) a triplet state lying above the $^1\Delta_g$ state of oxygen molecule (0.98 eV), and, consequently, a good singlet oxygen quantum yield (Φ_Δ).

Very recently, a class of already excellent dyes for applications of sensor and fluorescent imaging, BODIPY (Figure 1) and its aza derivatives, have emerged as possible PDT agents. The photophysical properties of some BODIPY derivatives have been computed by using density functional theory (DFT) and its time-dependent formulation (TDDFT) [1,2].

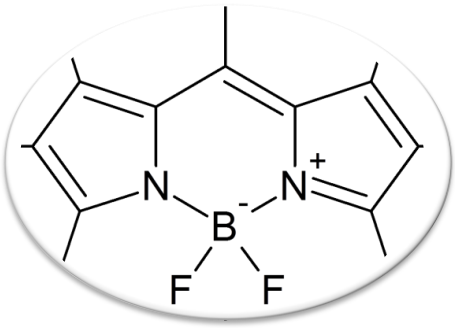

Figure 1: Basic structure of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY).

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POS-37

Microliter-scale sample pretreatment and multidetection chromatography for the analysis of endogenous benzoquinones

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Endogenous benzoquinones (i.e. coenzyme Q10) are crucial components of the mitochondrial respiratory chain, playing a pivotal role in cellular energy production [1]. Bioenergetic and antioxidant properties are strictly dependent on concentrations and redox state, thus analytical assays for both oxidized and reduced forms in biological samples are strongly required.

For this reason, an original and innovative analytical strategy has been developed to quantify benzoquinones by means of an analytical multidetection tandem setup, based on LC coupled to diode array detection (DAD) and electrochemical detection (ED).

Extensive preliminary assays on detection electrode potentials allowed the simultaneous quali-quantitative determination of oxidizable and reducible species. ED approach has shown to be highly sensitive and selective, leading to increased signal-to-noise ratios and minimal interference issues. On the other hand, a thorough absorption wavelength screening, allowed by DAD detection, showed high potential for peak purity studies. Analytical performances of the two detection means were compared in terms of selectivity, matrix effect and precision.

Due to the complexity of biological samples involving benzoquinone redox systems, a novel miniaturised pretreatment strategy has been developed in order to obtain effective and feasible sample purification from potential interfering compounds. Microextraction by packed sorbent (MEPS) represents an advancement over classical solid phase extraction, able to provide remarkable performances for the pretreatment of very low sample volumes. MEPS has shown to be a promising tool for microliter-scale biological samples, in terms of selectivity and extraction yields.

The developed method is under validation and these preliminary results have proven to be widely promising for quali-quantitative determination of oxidized and reduced forms of endogenous benzoquinones in complex biological systems.

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POS-38

New opportunities from the *ChIC* (Chitosan, Ionic Liquid, CO_2) three component system

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The reduction, fixation, and use of carbon dioxide (CO_2) is one of the major and urgent challenges the scientific community has demanded to address. Among the several strategies to face this problem, capture and storage of CO_2 in geological storages (for example saline aquifers or deep ocean storage) is considered at present the best option, while CO_2 utilization remains an underexploited opportunity [1].

Ionic Liquids (ILs) are organic salts which have attracted exponential interest in the last two decades due to their unique physicochemical properties, and to their capability to dissolve biopolymers (cellulose, chitin and chitosan) [2]. Among the biopolymers available in large amounts, chitosan, which is an aminopolysaccharide consisting of β-(1→4)-linked D-glucosamine units, is directly obtained by de-*O*-acetylation of chitin, the second most abundant biopolymer on earth after cellulose.

While ILs have been under investigation for quite some time as CO_2 capture systems, only a few recent reports studied CO_2, ILs, and chitosan, at the same time [3].

Herein the attempt to prepare an ureido cross-linked chitosan in ILs using CO_2 as the cross-linking agent is reported as a way to capture the greenhouse gas and modify the biopolymer at the same time. The new synthesized material was characterized by FT-IR studying the morphology by IR imaging. Finally, the thermal stability was studied by thermo gravimetric analysis (TGA) and compared with pristine chitosan.

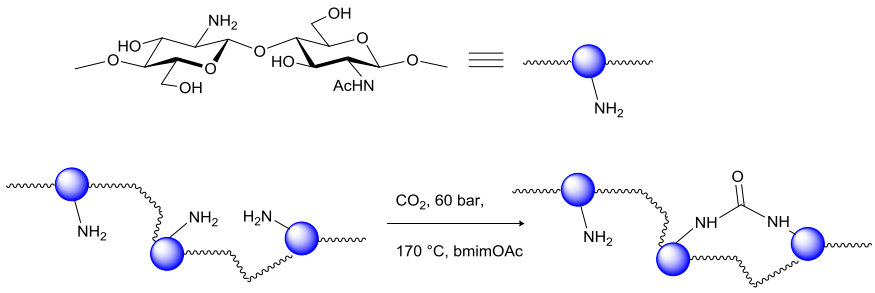

Figure 1: ureido cross-linked chitosan.

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POS-39

Modelling of nonlinear chemical reactions in giant liposomes: a step towards a batch pH-oscillator

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Giant lipid vesicles are commonly employed as cell models in different disciplines spanning from theoretical physics to membrane chemistry and membrane biology. More recently, lipid vesicles have been also proposed for studying nonlinear chemical reactions and chemical communication among compartments [1].

In this context, we chose to confine an enzymatic reaction, namely the urea-urease reaction, inside giant liposomes in order to design a batch pH oscillator [2]. The urea-urease reaction occurs in numerous cellular systems and is used by bacterium *Helicobacter pylori* in order to raise the local pH through the production of ammonia. In the proper conditions, this reaction could give rise to bistability, high steady state, low steady state and oscillations.

In order to simulate the dynamical behavior of the urea-urease reaction confined in a cell-like system, a two-variable model was initially derived in which acid and urea were supplied at rates k_H and k_S from an external medium to enzyme-containing compartment [3]. Oscillations were found provided that the condition $k_H > k_S$ was met. This two-variable model has been subsequently modified taking into account the product transport (k_N) and the hydrolysis of the probe (pyranine) encapsulated into the giant vesicles and used to monitor the pH changes. Here we present preliminary results obtained with the new model and compare these first simulations with the phase diagrams traced with the two-variable model.

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POS-40

One-pot cross-aldol condensation and intramolecular direct arylation for the rapid construction of π-extended thiophene and furan-based scaffolds

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Conjugated π-extended organic compounds based on aromatic heterocycles such as thiophene and furan are enjoying a continuously increasing popularity in the organic materials field. Their attractive properties at the molecular, supramolecular and macro-molecular level have prompted their use as organic materials in a plethora of applications, going from light-emitting diodes (OLED), to organic photovoltaic cells (OPVs) and organic field-effect transistors (OFETs) [1]. Incredible efforts have been devoted in recent years towards the development of complex molecular architectures able to afford more and more efficient and tunable materials, often at the expense of the scalability of the synthetic sequence, as well as its industrial suitability [2].

We report a regioselective and efficient one-pot cross aldol-Direct Hetero Arylation [3] strategy for construction of fully π-conjugated compounds in which thiophene or furan rings are fused to arene or heteroarene moieties. The described approach has its roots in the observation that both protocols are conducted in aprotic polar organic solvents, and require relatively weak bases to function. Two alternative synthetic strategies were used (see Figure), differing from the relative positioning of the aldehyde and electron-withdrawing group involved in the aldol condensation. In first case (a), isatin derivatives fused with thiophene and furan rings (structures A and B) were obtained in good yields. Following approach b), a series of naphtothiophenes and naphtofurans were obtained in even higher yields, by developing the use of a carboxylic acid functionality as EWG (Structures C and D), followed by esterification by alkylation, with all three synthetic steps of the sequence conducted one pot. Although C and D have been previously reported, our methodology allowed much improved yields, and a substantial reduction of the synthetic steps with respect to the previously published ones. Our results indicate that the one pot combination of different synthetic methodologies can be the key to ensure industrial scalability for the synthesis of polycyclic, π-extended compounds, useful as organic materials.

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[3] L. G. Mercier and M. Leclerc, *Acc. Chem. Res.* **46** (2013) 1597-1605.

POS-41

Mechanochemical oxidation of perfluoro anilines to perfluoro azobenzenes

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Aromatic azo compounds have been widely used in industrial applications mainly as organic dyes and pigments, but also as indicators, food additives, and therapeutic agents [1]. Several synthetic strategies to afford symmetric azo compounds are known [2], the most used concern the oxidative coupling of aromatic amines or the reductive homodimerization of nitroarenes. In order to achieve satisfactory yields in the electron-poor aromatic amines omocoupling reaction, the use of stoichiometric toxic and environmentally unfriendly transition-metal based oxidants is often necessary. On the route to target polyfluorinated heteroaromatic systems, we needed an efficient method to gain symmetric polyfluoro azobenzenes and this has been achieved in satisfactory yields by oxidation of polyfluoroanilines with environmentally friendly oxidants under solventless mechanochemical technique [3].

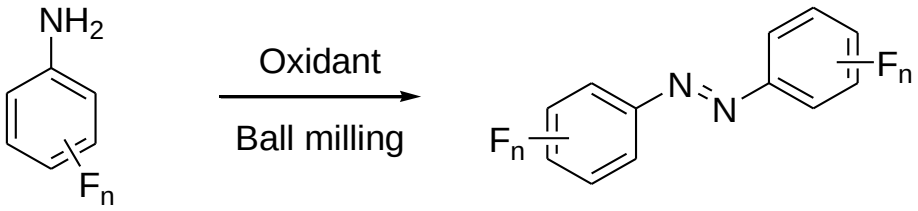

Figure 1: Reaction scheme of oxidative coupling of aromatic amines.

Here we report our study on the preparation of polyfluoro azobenzenes using $Ca(OCl)_2$ and $Ph\text{-}I(OAc)_2$ in a zirconia mill, evaluating also the effect of silica as inert grinding auxiliary on the reaction outcomes and easiness of working up. Best yields in polyfluoro azobenzenes have been obtained with highly fluorinated starting anilines.

[1] K. Hunger, P. Mischke, W. Rieper, R. Raue, K. Kunde and A. Engel, "Azo Dyes" in "Ullmann's Encyclopedia of Industrial Chemistry", Wiley-VCH, Weinheim, 2005.
[2] E. Merino, *Chem. Soc. Rev*. **40** (2011) 3835-3853.
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POS-42

Fast, green and alternative synthesis of a precursor for automated nucleophilic [^{18}F]-L-DOPA production

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[^{18}F]-L-DOPA is an established radiotracer used for diagnosis of integrity of nigrostriatal dopaminergic system, head cancer and neuroendocrine tumors by PET. [^{18}F]-L-DOPA may be prepared successfully by full automated nucleophilic radiosynthesis process [1] starting from a precursor (S-3-(5-Formyl-4-methoxy-2-nitrophenyl)-2-(trityl-amino)-propionic tert-butylester) [2]. The synthetic process of precursor is long, difficult and with low yield.

A shorter, more efficient and environmentally friendly synthesis of a new hypothetic precursor for automated module by oxidation [3] and nitration of natural products was developed.

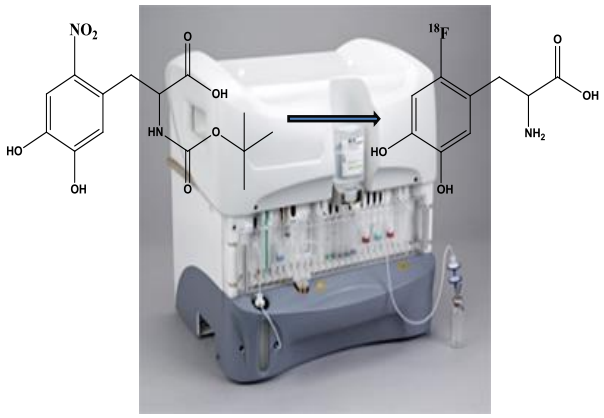

Figure 1: Automated synthesis of [^{18}F]-L-DOPA starting by a new nitrated precursor.

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[3] R. Bernini, M. Barontini, F. Crisante, M. C. Ginnasi and R. Saladino, *Tetrahedron Lett.* **50** (2009) 6519-6521.

POS-43
Catalytic oxidative desulfurization of a model fuel

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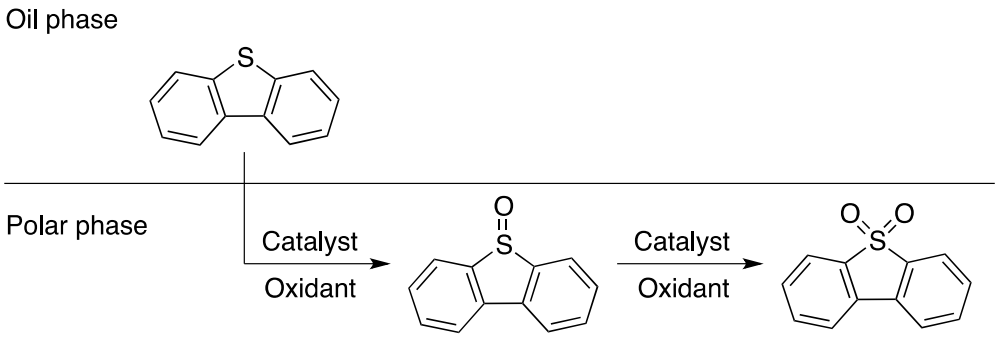
We report the effective and efficient synthesis of a titanium oxide-based catalyst on a commercial silanized silica network. The material proved to be an active catalyst for batch and flow organosulfur oxidation processes of liquid fuels [1] allowing the selective oxidation of dibenzothiophene to the corresponding sulfone using hydrogen peroxide as oxidant, in acetonitrile under metal-free conditions.



Preliminary tests with the unsilanized catalyst led to a good conversion of the substrate. However, we noticed a rapid deactivation of the catalyst probably due to the adsorption of the polar product on the catalyst surface. Therefore, we decided to silanized the catalyst [2].

Under optimized conditions, the silanized catalyst showed very good catalytic activity and an excellent conversion, but still a low durability if used in combination with hydrogen peroxide as oxidizing agent. Replacing hydrogen peroxide with TBHP, we finally reached complete conversion and demonstrated that in these conditions the catalyst could be reused for several times both in batch and in flow without any intermediate treatment.

More studies are focused on the up scale of this catalytic method, screening a real fuel containing different organosulfur groups as substrates.

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POS-44

Quality by design in the optimization of a nanosystem-ethosomal formulation for topical treatment of vitiligo

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Quality by Design (QbD) is a fundamental pharmaceutical quality model to be considered in the development of pharmaceutical products and processes, introduced by FDA and supported by ICH. A new and innovative thymoquinone-loaded vesicular system for the treatment of vitiligo was carried out following QbD principles. Thimoquinone (TQ) is a natural bioactive compound, which is extracted from *Nigella Sativa* seeds, with many therapeutic properties. Ethosomes composed of phospholipid, ethanol and water obtained by thin layer evaporation technique resulted the suitable nanocarriers for enhanced transdermal drug delivery. Influential factors were classified in different categories (formulation, process, method, environment) and critical process parameters were selected. Critical quality attributes were represented by vesicle size (size), dimensional uniformity (PDI) and encapsulation efficiency of TQ (EE%). Size and PDI studies were carried out using dynamic light scattering, while EE% was evaluated by a fast capillary electrophoresis method assaying the free TQ after ultracentrifugation. Experimental design tools made it possible to better understand the interactions among all the variables and to obtain the appropriate Design Space (DS). A three factors design allowed the contour plots to be drawn and the DS to be defined in combination with Monte-Carlo simulations. The DS was visualized by means of probability maps and included all the operative conditions, which led to fulfill the requirements of the quality product with a degree of probability $\pi \geq 90\%$. *Ex vivo* studies were carried out by Franz diffusion cells and pointed out that the TQ-loaded ethosomal system improved the penetration of TQ into the skin.

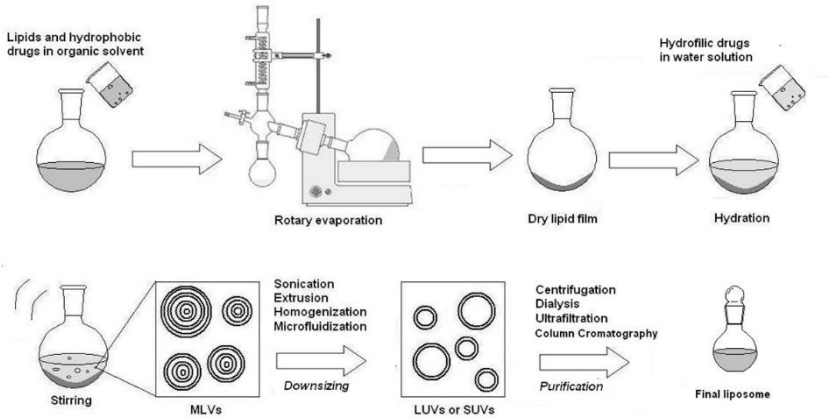

Figure 1: The thin layer evaporation technique of ethosomes.

POS-45

Antioxidant activity and chemical characterization of natural bioactive compounds

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The Bioactive Compounds (BCs) are natural substances which have the capability to interact with one or more component(s) of the living tissue, with the possibility of generating a wide range of effects [1]. Among the main classes of BCs, a relevant role is played by the antioxidant substances: any substance that, when present at low concentrations compared to those of an oxidisable substrate, significantly delays or prevents the oxidation of a given substrate [2]. These substances also show different and important biological properties, that are of interest in the cosmetic, pharmaceutical and especially in the food industries as biopreservatives.

Among the large variety of BCs with antioxidant properties, we focused our attention on those obtained from some Abruzzo's territory officinal plant species. From these matrices we recovered the Essential Oils (EOs) by the conventional steam/hydro-distillation, and we produced water and/or ethanolic extracts by the Rapid Solid-Liquid Dynamic Extraction (RSLDE), an extraction technique performed by the Naviglio Extractor®, an innovative device for the production of natural extracts [3].

For all the EOs and RSLDE extracts were carried out: (i) the assessment of their antioxidant capacity (AOC) and their total phenolic content (TPC), evaluated *in vitro* using different spectrophotometric assays: ABTS/TEAC, FRAP, DPPH and Folin-Ciocalteu, respectively, and (ii) the investigation of their chemical composition.

The AOC and TPC analysis, showed good results for all EOs tested. Among the extracts the best results were observed for *T. vulgaris* (TEAC/ABTS: 31,2 ± 1,9 μmol Trolox/g dw; Folin-Ciocalteu: 157.5 ± 26.4 mg GAE/g dw). The GC-MS chemical characterization of the EOs revealed as main compounds: diallyl trisulfide (45%) and diallyl disulfide (35%) for *A. sativum*; myrcene (49%) for *C. sativa*; linalool (80%) for *C. sativum*; camphor (18%), borneol (16%), 3-carene (13%) and eucalyptol (10%) for *R. officinalis*; thymol (42%) and 3-carene (20%) for *T. vulgaris*. For the RSLDE extracts we optimized a convenient concentration and a clean-up procedure, in order to be able to investigate their chemical composition by different chromatographic techniques. The results obtained, indicate the potential of the tested EOs and extracts for an application as food preservatives.

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POS-46

A novel, efficient mechanism for coupling high performance liquid chromatography with electron ionization mass spectrometry

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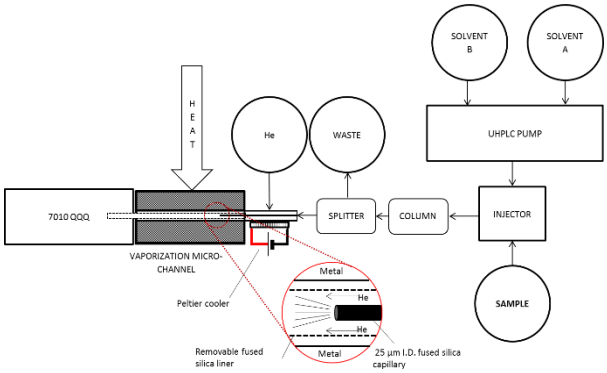
Unknown identification is of increasing importance in a wide range of investigation areas where the presence of non-targeted compounds represents a key factor. Liquid chromatography coupled to mass spectrometry (LC-MS) represents one of the most versatile tool for target and non-target analyses and has become the technique of choice in routine analysis [1].

A novel liquid chromatography-mass spectrometry (LC-MS) interfacing concept is presented. The new interface, called Liquid-EI (LEI), is based on electron ionization (EI) but, differently from any previous attempt, the vaporization of solutes and mobile phase takes place into a specifically designed chamber called vaporization micro-channel, before entering the high-vacuum ion source [2]. The interface is completely independent from the rest of the instrumentation and can be adapted to any GC-MS system, as an add-on for a rapid LC-MS conversion. A ceramic liner, placed inside the vaporization micro-channel, acts as an inert, smooth vaporization surface speeding up the gas-phase conversion of large molecules while lessening possible memory effects. The liner is a throwaway commercial component easy to replace. A Helium gas flow surrounds the inner capillary and speeds up the transport of the vapours into the ion source. A Peltier unit is used to avoid undesired early vaporization before entering the interface. The rapid vaporization offered by the lined micro-channel reduces the chance of thermal decomposition and broadens the range of suitable applications, especially those regarding non-targeted analytes. High-quality, library-searchable mass spectra are thus generated.



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POS-47

Investigation of cytotoxic effects of different ZnO nanostructures on living cancer cells

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Thanks to its intrinsic and unique physico-chemical properties, in recent years the use of zinc oxide (ZnO) has increased for applications in different fields, from biosensing to cancer therapy. Besides, ZnO is known to be a versatile material, easy to synthesize in different shapes and sizes, as nanowires and nanoparticles [1]. Those nanostructures can be in turn effortlessly functionalized with many types of chemical molecules, in order to improve their bioavailability and related functionalities. Obviously, their dimensions as well as the possible presence of surface functional groups can dramatically modify their behavior in a biological context, as living cell culture, and the understanding of these mechanisms is still crucial for exploiting ZnO nanostructures as therapeutic and/or diagnostic agents [2]. In this study the cytotoxic behavior of different ZnO nanostructures was *in vitro* evaluated analyzing the long-term responses (until 72 hours) of the tumor KB cell line (human oral carcinoma). Cells were cultured with different concentrations of bare ZnO nanoparticles (ZnO NPs) and nanowires (ZnO NWs), and amino-propyl functionalized ZnO nanoparticles (ZnO-NH_2 NPs) [3]. We directly imaged the ZnO-NH_2 NPs and ZnO NWs cytotoxic effect through transmission electron microscopy (TEM), even if without getting a clearly evidence of their presence and localization into the cells, due to both their low amount and size. Our results demonstrate however that the different morphology and surface functionalization of ZnO nanostructures could differently affect the cell growth. In particular, an apparent viability decrease of cells treated with ZnO NWs was observed, and TEM analyses also showed that both ZnO NPs and ZnO NWs could generate severe damages in KB cells just after 5 hours of incubation. Conversely, the presence of the ZnO NPs surface functionalized with aminopropyl groups looked mitigating the cytotoxic effect more clearly than what observed with bare ZnO NPs.

[1] P. Zhu, Z. Weng, X. Li, X. Liu, S. Wu, K. Yeung, X. Wang, Z. Cui, X. Yang and P. Chu, *Adv. Mater. Interfaces* **3** (2016) 1-30.
[2] J. Rasmussen, E. Martinez, P. Louka and D. Wingett, *Expert. Opin. Drug. Deliv.* **7** (2010) 1063-1077.
[3] V. Cauda, R. Gazia, S. Porro, S. Stassi, G. Canavese, I. Roppolo and A. Chiolerio, "Handbook of Nanomaterial Properties. XXVII", Springer Verlag, Berlin Heidelberg, 2014.

POS-48

Synthesis of monoalkyl glyceryl ethers through reaction of glycidol with alcohols in presence of Lewis acids

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The present work deals with the preparation of monoalkyl glyceryl ethers (MAGEs) through homogeneously-catalyzed etherification of glycidol (2,3-epoxy-1-propanol) with alcohols.

Monoalkyl glyceryl ethers have already found several applications such as in the formulations of inks, lubricants, polymers, detergents and as building-block of anti-inflammatory compounds and 1,3-dioxolan-2-ones [1].

Recently [2], we have suggested an innovative reaction pathway to synthetise glycidol through the conversion of 2-chloro-1,3-propanediol, a by-product in the industrial production of epichlorohydrin from glycerol. As a result, the production of glycerol ethers from glycidol becomes more interesting.

In this work, we report on the ring-opening reaction of glycidol with different alcohols (ethanol, methanol, 2-propanol, tert-butanol, 1-butanol, 1-pentanol, 1-ottanol and benzyl alcohol) and different Lewis acids ($BiCl_3$, $AlCl_3$, $FeCl_3$, $FeCl_2$, $ZnCl_2$, $Bi(OTf)_3$, $Al(OTf)_3$, $Fe(OTf)_3$, $Fe(OTf)_2$, $Zn(OTf)_2$) as catalyst (Figure 1).

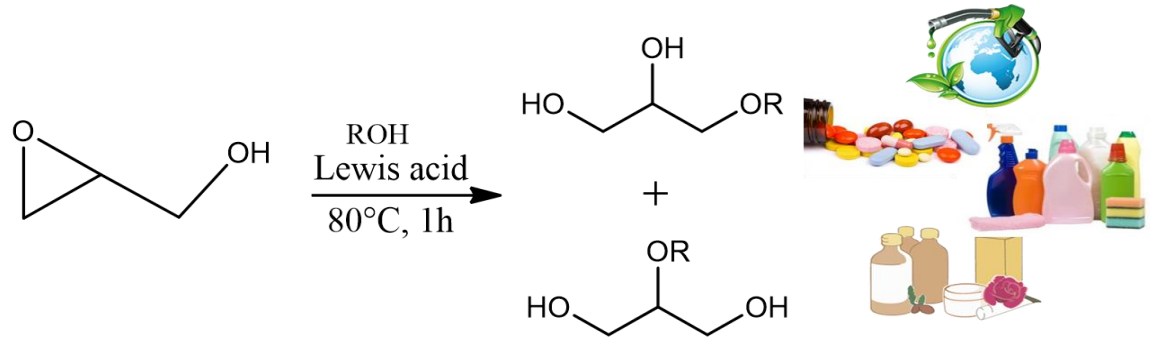

Figure 1: Homogeneously-catalyzed etherification of glycidol with alcohols.

Results show that metal triflates such as $Al(OTf)_3$ are able to catalyze the reaction of glycidol with alcohols at 80°C in 1 h using a catalyst loading of 0.01 % in moles. Moreover the monoethyl glyceryl ethers are obtained with high selectivity (>90%) and conversion (100%).

[1] M. Sutter, E. Da Silva, N. Duguet, Y. Raoul, E. Metay and M. Lemaire, *Chem. Rev.* **115** (2015) 8609-8651.
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POS-49

Effect of water on the nanostructure of alkylammonium based ionic liquids

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A series of mixtures of butylammonium butanoate $[N_{0\ 0\ 0\ 4}][C_3CO_2]$ and butylammonium nitrate $[N_{0\ 0\ 0\ 4}][NO_3]$ in water has been prepared with different molar fraction to see the effect of water on the nanostructural order present in both of the ionic liquids. Small and wide angle X-ray scattering (SWAXS) patterns of $[N_{0\ 0\ 0\ 4}][C_2CO_2]$ and $[N_{0\ 0\ 0\ 4}][NO_3]$ in neat state show strong prepeak at smaller Q value, which is associated with the aggregation of nonpolar butyl chains on both cation and anion. At lower concentration of water the mixtures show significant prepeaks but at higher water content, above 90% concentration of water the prepeaks starts to disappear which indicate the separation in the alkyl chains due to strong intermolecular interaction between polar ends of cation and anion with water. The most remarkable shift in peaks is observed in the mixtures of $[N_{0\ 0\ 0\ 4}][C_3CO_2]$ than of the $[N_{0\ 0\ 0\ 4}][NO_3]$. To reproduce the structural pattern molecular dynamic (MD) simulations has been performed for the whole series of mixture which present results in good agreement with that of the experimental.

POS-50

Self-assembling luminescent water-soluble Ir(III) ionic complexes

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Novel luminescent water-soluble Ir(III) complexes **[(*ppy*)$_2$Ir(*bpy*)]X** (**X**$^-$ = EtO$^-$, OH$^-$, EtOCH$_2$CO$_2^-$, MeOCH$_2$CO$_2^-$) have been synthesized, presenting self-assembling properties at high concentration in water leading to a gelification process. The luminescent properties of the complexes in water have been investigated through steady state and time-resolved photophysical studies showing the instauration of two specific aggregations-types responsible for the formation of the gel phase [1]. The gel phase observed under polarizing optical microscope is characterized by a homogeneous and birefringent texture, indicative of an ordered anisotropic phase.

Through PXRD analysis, performed on the gel phase and the xerogel thin film, it has been possible to determine the architecture of the supramolecular organization. The gel phase is constructed of tetragonal columnar strands formed by Ir(III) cations, which are furtherly self-assembled in an oblique system. These Ir(III) complexes implement the pool of metallogels, a new class of multifunctional soft materials currently receiving particular attention [2].

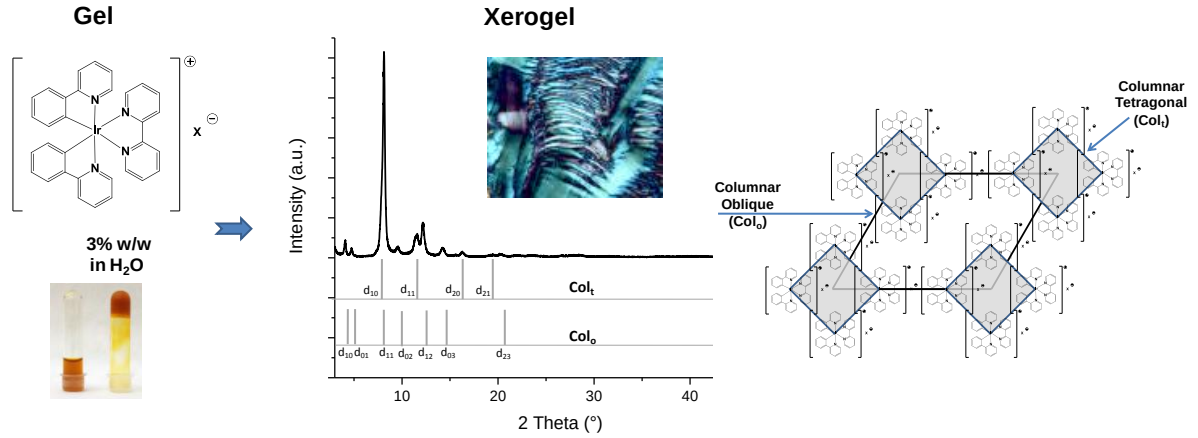

Figure 1: Supramolecular architecture of self-assembling Ir(III) complexes in water.

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POS-51

Improving the stability of light-emitting electrochemical cells based on heteroleptic [Cu(N^N)(P^P)]$^+$ complexes

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Nowadays, ionic transition metal complexes based on copper (I) are a cheap alternative to iridium (III) complexes for light-emitting electrochemical cells (LECs). In particular, heteroleptic copper(I) complexes belonging to the [Cu(N^N)(P^P)]$^+$ family exhibited promising results [1]. Therefore, we decided to synthesize, characterize, and compare in LECs two Cu(I) complexes, namely [Cu(2,2'-bipyridine)(POP)]PF_6 (**1a**) and Cu(2,2'-bipyridine)(6,6'-dimethoxy)(POP)]PF_6 (**1b**) [2].

We effectively proved that the device performances of **1b** are better than those of **1a**. In particular, we obtained a 3 times higher efficiency together with an extended lifetime under pulsed current. At this point, we decided to further improve the stability of the device by using the organic 4,4′-Bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) to perform a host-guest system. Here, a 10 times higher lifetime was observed along with a lower driving voltage, while the luminance remained comparable.

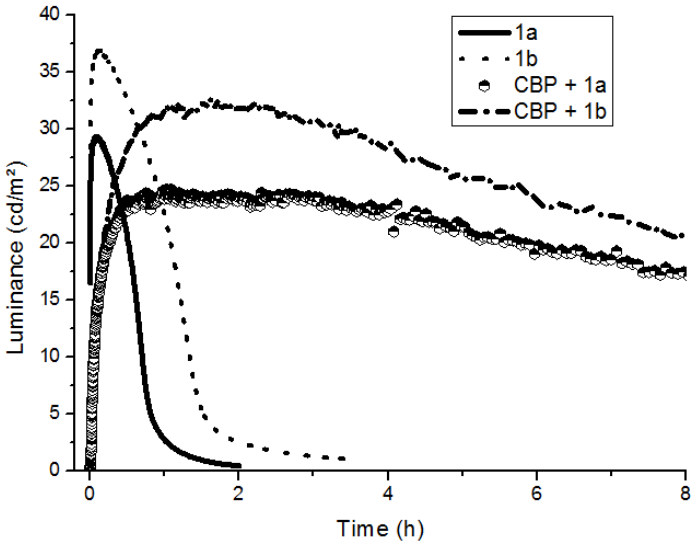

Figure 1. Luminance vs time graph for the various devices under PC (7.5 mA).

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[2] our paper (to be submitted soon).

POS-52

The QTrap approach in "emerging" marine lipophilic toxins analysis

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Marine lipophilic toxins (MLTs) are toxic compounds produced by secondary metabolism of marine microalgae; they often accumulate in mussels representing a risk to consumers health. Okadaic acid, dinophysistoxins, pectenotoxins, yessotoxins and azaspiracids (AZAs) are regulated MLTs. AZAs have never been reported in Mediterranean seafood until now. Cyclic Imines - CIs (including Spirolides - SPXs and Gymnodimines - GYMs) are considered "emerging" toxins worldwide not yet regulated. This work aims to investigate AZAs and CIs in mussels by hybrid triple-quadrupole/linear ion trap mass spectrometry. Samples from mid-Adriatic sea (Italy) were analysed using the modified LC-MS/MS protocol for marine lipophilic toxins [1]. This method allows also the analysis of CIs. Two types of experiments were conducted: a Multiple Reaction Monitoring (MRM) selecting two transitions for each molecule and an Enhanced Product Ion (EPI) scan using the linear ion trap (LIT). The EPI enables the MLTs identity confirmation by comparison of the sample fragmentation pattern with literature data and certified standards mass spectra. Traces of AZA2 were for the first time detected in Mediterranean seafood as already reported in Toxicon [2]. Two SPX analogues (13-desMeC SPX and 13, 19-didesMeC SPX) and GYM A (first report in Italy) were measured in mussels with a maximum concentrations of 25 µg/kg (sum of the 2 analogues) and of 12 µg/kg respectively. This approach proved to be useful for the investigation of the emerging marine toxins in mid-Adriatic sea.

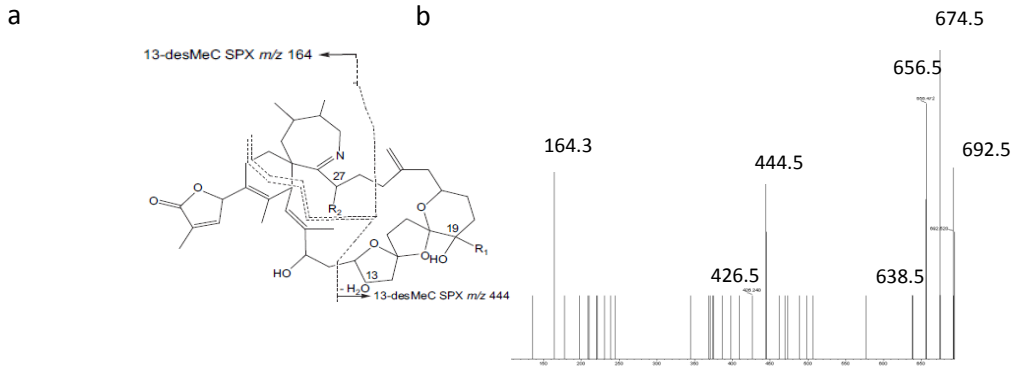

Figure 1: Fragmentation pathway of 13-desMeC SPX(a), EPI spectrum of a sample (b).

[1] AESAN Agencia Española de Securidad Alimentaria y Nutrición. EU-Harmonised Standard Operating Procedure for determination of Lipophilic marine biotoxins in molluscs by LC-MS/MS vers. 5, 2015.
[2] S. Bacchiocchi, M. Siracusa, A. Ruzzi, S. Gorbi, M. Ercolessi, M. A. Cosentino, P. Ammazzalorso and R. Orletti, *Toxicon* **108** (2015) 115-125.

POS-53

Photoinduced nitric oxide selective release in mitochondria

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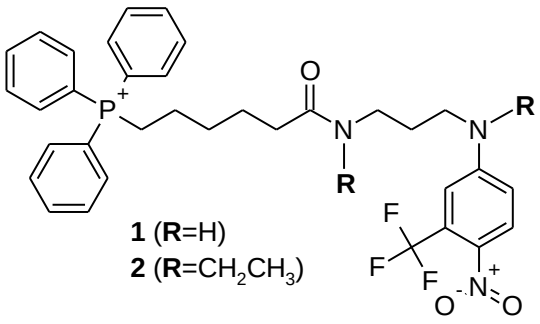
Nitric oxide (NO) is a ubiquitous and pleiotropic messenger; it plays a variety of roles in human physiology and pathophysiology; it displays its cytotoxic effects in mitochondria directly, e.g. by inhibiting respiration and the citric acid cycle, or indirectly, producing reactive nitrogen species (RNS) by reacting with oxygen and superoxide anion (O_2^-). In particular this latter reaction affords peroxynitrite (^-OONO), which in turn gives rise to two very reactive and toxic radicals: $OH^{\cdot}$ and $NO_2^{\cdot}$. This induces damage to proteins and activation of mitochondrial pathways of apoptosis [1].

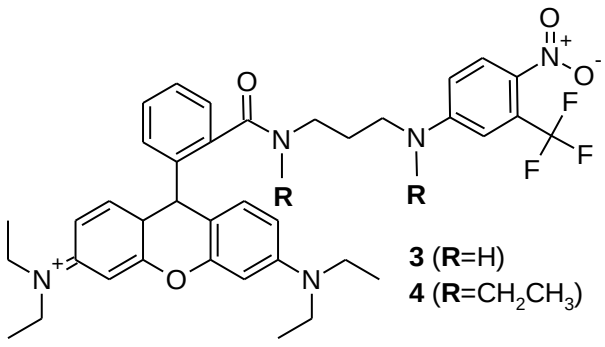
In human solid tumour there are hypoxic regions that have lower oxygen concentration than normal tissues; this imparts resistance to radiotherapy, chemotherapy and photodynamic therapy. So there is a great attention to NO-donors as anticancer agents and, among them, to NO-photodonors since they allow an accurate control of the timing, location and dosage of NO-released.

Each of two photo-responsive NO donors chosen, N-(3-aminopropyl)-4-nitro-3-(trifluoromethyl)-aniline and N,N'-diethyl derivative, was linked to two different mitochondrial-targeting ligands, Triphenylphoshonium and Rhodamine, in order to obtain new multifunctional compounds (**1**, **2**, **3**, **4**). In lung epithelial cells these compounds shown a mitochondrial targeting and, after light irradiation, they can release NO in a concentration able to cause a higher cytotoxicity than the NO-photodonors alone.

The synthesis, physico-chemical characterization, cell tests and the potential application of these compounds will be discussed.



1 (**R**=H)
2 (**R**=CH_2CH_3)



3 (**R**=H)
4 (**R**=CH_2CH_3)

[1] J. Morgan and A. R. Oseroff, *Adv. Drug Deliv. Rev.* **49** (2001) 71-86.

POS-54

Development of enzyme-based microsensors for *in* and *ex vivo* analyses

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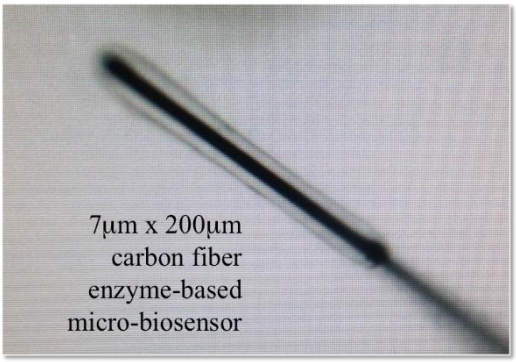
Nowadays real-time quantitative measurements of many proteins, metabolites and cancer biomarkers, are feasible by the use of biosensors for *in vitro* and *in-ex vivo* studies [1]. Although, strategies on biosensor design are rapidly increasing, enzymatic biosensors remain a large and important field of study. Enzymes achieve molecular recognition of the substrate based on structural complementarity and exploit an analyte-dependent step to convert an electrochemically inert substrate to an active product, often revealing high selectivity, sensitivity and time scale. Even if, amperometric biosensors have been around since the early 1960s [2-3], it is the production of very tiny micro-electrode biosensors that offers great utility for studying chemical signalling for *in vitro* (single cells) and *in-ex vivo* studies. These microelectrode biosensors have the advantage of offering a better spatial and temporal resolution and they are considerably less invasive than other electrodes. The miniaturization of biosensors is challenging, as they need to be both extremely small and highly sensitive. In fact, smaller is the sensor, smaller is the electrode surface area, and consequently the recorded amperometric signal diminishes [1]. The requirement in miniaturizing biosensors is to maintain a signal to noise ratio that enables effective and sensitive detection of the analyte. The tiny sensing surface of the sensor has to be coated with a high density of enzymes in their native active conformation. Furthermore, for *ex vivo* analyses, it is mandatory to control the selectivity of the signal and the mechanical strength of the sensor itself, which has to enter in tissues without damaging. In this work, we present the development of thin, robust and highly active micro-electrode enzymatic biosensors for detecting metabolites, such as glucose, lactate and ATP in tissues.



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POS-55

Micro tips-SPME pre-treatment procedure for the analysis of nandrolone, clostebol and methandrostenolone in urine microsamples by LC-MS/MS

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Illegal anabolic androgenic steroids (AAS) are probably the most frequently abused drugs within the frame of professional and amateur sport competitions. For this reason, rapid and reliable sampling and pre-treatment procedures are needed if steroids are to be unequivocally identified in biological samples, even when present at very low concentrations or when sample volume is extremely limited.

For this purpose, an innovative purification procedure has been developed for application to urine microsamples. The procedure is based on Micro Tips-SPME (Solid-Phase MicroExtraction) and allows analyte adsorption from aqueous samples on a fiber, followed by LC analysis.

The sampling fiber can be polymeric (relatively hydrophilic) or octadecyl-coated (lipophilic), according to the chemical-physical characteristics of the AAS to be determined. The chosen fiber is used in static conditions: conditioning is carried out with methanol, while sample adsorption is carried out by immersion urine microsample. Desorption is ultrasound-assisted, by immersion in methanol.

Since this is an equilibrium technique, fine-tuning of several experimental conditions (temperature, immersion times and saturation) is of the utmost importance and has been carried out to obtain satisfactory results with the identification of heavily-abused exogenous AAS such as nandrolone, clostebol and methandrostenolone in urine samples spiked with the analytes. The feasibility and need for minute amounts of sample (up to 100 µL of urine) make this procedure ideally suited for coupling to high-throughput LC-MS/MS analysis, especially for the detection of exogenous AAS, whose mere presence in urine is considered as an "adverse analytical finding" by the World Antidoping Agency (WADA) [1].

Method validation according to international guidelines is now underway, but preliminary results are very encouraging.

This research was funded by Grant J52I14001600005 (Italian Ministry of Health, section for the monitoring and control of doping and the protection of health in sporting activities of the health technical committee).

[1] World Anti-Doping Agency (WADA), "Prohibited list", 2016.

POS-56

Soft synthesis and detemplation of carbon-based hexagonally ordered hierarchical mesoporous sieves FDU-15

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A series of hydrophobic carbon-based FDU_15 mesoporous materials were synthesized by thermo polymerization of phenol formaldehyde resins (resols). The ordered carbon sieves were prepared under basic conditions at 70ºC, using triblock (poly (ethylene glycol)-poly (propylene glycol)-poly (ethylene glycol)) copolymer Pluronic P123 as structure directing agent in a soft solvothermal synthesis approach. Hexadecane was used as swelling agent in order to tune the pore size of the materials [1]. Surfactant and co-surfactant removal was preliminarily carried out by solvent extraction using a sonochemical methodology. After template removal. the synthesized hierarchical sieves were pyrolyzed under a constant flow of nitrogen to remove the residual surfactant and yield a carbon-based material. The porosity, hexagonal ordering and morphology of these hierarchical structres were determined by SAXS, SEM, TEM and N_2 physisorption techniques. These materials are expected to be used as a Pt catalytic support for electrochemical applications.

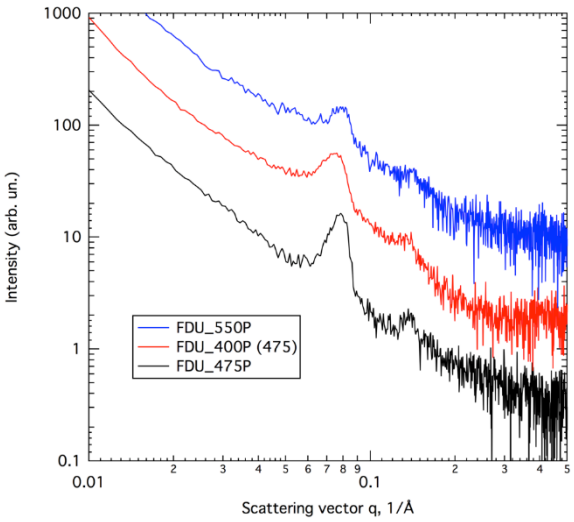

Figure 1: SAXS patterns for FDU samples. The curves are arbitrarily shifted on the y-axis for the sake of clarity (50W, 600sec of acquisition time).

[1] F. Zhang, Y. Meng, D. Gu, Y. Yan, Z. Chen, B. Tu, D. Zhao, *Chem. Mater*. **18** (2006) 5279-5288.

POS-57

Nanochemical strategies for improving the photoactivity of colloidal TiO_2: doping and sensitization

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[d] *Istituto di Nanotecnologia, Consiglio Nazionale delle Ricerche, Via Orabona 4, 70125-Bari, Italy*
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TiO_2 nanocrystals (NCs) have a well-known strategic role in environmental photo-catalysis and photo-electrochemical solar energy conversion. However, because of the wide band gap, this material can absorb almost only the ultraviolet region of the solar spectrum, *i.e.* less than the 5% of the total energy reaching Earth. Several approaches were proposed in the last decades in order to extend TiO_2 NCs photoactivity in a wider spectral range. We explored two nanochemical strategies for this purpose.

On one hand, we resorted to a colloidal chemistry route based on an alcoholysis reaction [1] to synthesize pure anatase, highly crystalline, iron-doped TiO_2 NCs with dopant content up to 20%. Substitutional iron(III) ions introduce new electronic states inside the band gap of TiO_2, inducing visible light absorption and thus extending the potential photoactivity of the material in this spectral region. Furthermore, iron doping facilitates the formation of oxygen vacancies in TiO_2 lattice and surfaces, which introduce more defect states, further improving visible light absorption [2].

On the other hand we tried to enhance TiO_2 NCs photoactivity by sensitization with small lead sulfide (PbS) nanocrystals, which show peculiar size-dependent optical absorption in the near-infrared range [3]. We produced the PbS/TiO_2 nanocomposites relying again to colloidal chemistry, through the epitaxial seeded-growth of PbS crystalline domains onto the surface of previously prepared TiO_2 NCs. This strategy provides intimate contact between the two materials and hence low inter-particle charge transport barriers.

We present structural, morphologic and spectroscopic evidence supporting the light-harvesting enhancement in the two model systems, offering useful insights for the design of new materials with potential application in photo-electrochemical devices.

[1] L. De Trizio, R. Buonsanti, A. M. Schimpf, A. Llordes, D. R. Gamelin, R. Simonutti and D. J. Milliron, *Chem. Mater.* **25** (2013) 3383-3390.
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POS-58

Target fishing of novel antifungal macrocyclic compounds

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Candida species are one of the most common causes of nosocomial bloodstream infections. Nowadays the large use of antifungal agents has led to the development of drug-resistant or even multi-drug-resistant fungal strains [1].

In the last ten years, our research group puts effort into the discovery of a new therapeutic class of antifungal agents, the macrocyclic amidinoureas [2].

A new synthetic approach for the synthesis of the compound **A** was performed (**Figure 1**).

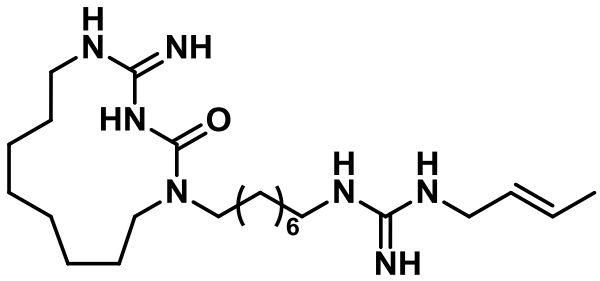

Figure 1: Compound **A**

To understand the mechanism of action of the compound **A** on *C. albicans*, whole genome transcriptional profile experiments were performed in the presence and absence of sub-inhibitory concentrations of this compound. Up-regulated genes exhibited typical signature for *TAC1*-regulated genes. *TAC1* is itself up-regulated as well as its target genes such as *CDR1* and *CDR2* (ATP binding cassette transporters). Their up-regulation was verified by separate RT-qPCR analysis. To investigate the relationship between our compound and these transporters, we measured the susceptibility to **A** of *C. albicans* mutants lacking both *CDR1* and *CDR2* [3].

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[3] D. Deodato, G. Maccari, F. De Luca, S. Sanfilippo, A. Casian, R. Martini, S. D'Arezzo, C. Bonchi, F. Bugli, B. Posteraro, P. Vandeputte, D. Sanglard, J. D. Docquier, M. Sanguinetti, P. Visca and M. Botta, *J. Med. Chem.* **59** (2016) 3854-3866.

POS-59

Novel polymer electrolytes based on poly(tetrafluoroethylene) with fluorophilic ionic liquids

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Poly(tetrafluoroethylene) (PTFE) has been acknowledged as a tolerant polymer owing to its low surface free energy. However, the inertness of PTFE unfavorably restricts preparations of stable composites with liquid materials such as electrolyte solutions. In order to prepare polymer electrolytes based on PTFE, electrolyte solutions having high compatibility with PTFE are needed to be designed. Ionic liquids (ILs), low-temperature molten salts, have been recognized as potential additive salts, because they are mainly composed of organic ions possessing structural diversity. In this study, novel ILs having fluorophilic function have been designed with intent of high compatibility with PTFE. Preparation of their composites and evaluation of electrochemical properties have been carried out.

Perfluorohexane (C_6F_{14}) was used as a model compound of PTFE and its solubility in various ILs was measured to evaluate fluorophilicity of ILs. Conventional ILs such as 1-ethyl-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide ([C_2mim][Tf_2N]) were found to dissolve C_6F_{14} less than 26.0 mmol mol^{-1}. This number was found to increase with increase in number and length of fluoroalkyl chain in ILs. Then, trihexyl(heptadecafluoroundecyl) phosphonium [Tf_2N] ([P_{666F}][Tf_2N]), having fluoroalkyl moieties not only on anion but also on cation, has been designed. Indeed, the solubility of C_6F_{14} in the ILs was improved to 420.5 mmol mol^{-1}. Then, the composites were prepared by mixing PTFE powder and these ILs in ratio of 1:1 (w/w).

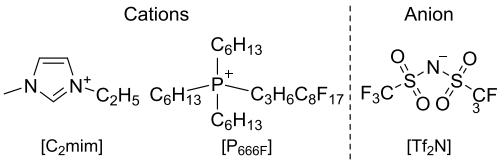

Figure 1: Structure of ILs.

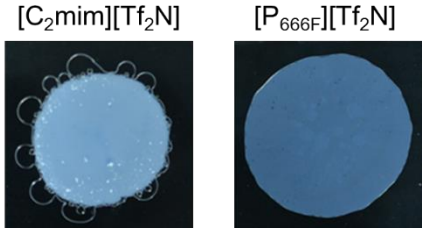

Figure 2: Pictures of PTFE-IL composites pressed with two glass plates with 0.05 mm spacer.

As shown in Figure 2 (left), non-functionalized [C_2mim][Tf_2N] were repelled from PTFE matrix. On the other hand, ILs functionalized with fluoroalkyl chain, i.e. [P_{666F}][Tf_2N], enable the preparation of homogeneous composites based on PTFE which did not accompany the bleed out of the ILs (Figure 2, right). The composites of PTFE and [P_{666F}][Tf_2N] were proposed for electrochemical analysis, and a suitable ionic conductivity was found for the composites. Further electrochemical properties will be characterized and shown at the presentation.

POS-60

Solution properties and DNA binding of Rh(III)-ciclopentadienyl-pyridinyl-quinoline complexes

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Among the wide efforts devoted by the scientific community to the design of new drugs with enhanced properties, studies have also focused on half-sandwich Rh(III) anticancer complexes, which can attack biosubstrates or perturb the redox status of cells [1,2]. In this frame, thanks to the long lasting collaboration between our groups, we are performing studies on the mechanistic aspects of the binding of especially devised metal complexes to biosubstrates as DNA, RNA and proteins [3].

In this work, we studied the interaction between the Iridium complex shown in Figure 1 and DNA. The chloride exchange process to give Rh-H_2O from Rh-Cl was assessed together with the acidity constants of Rh-H_2O. Then, the possible binding reaction of the two species Rh-H_2O and Rh-OH^- with DNA was analysed making use of different approaches ranging from spectrophotometry, viscometry, circular dichroism until stopped-flow kinetics. The obtained results indicated that the interaction does indeed occur and its different features will be discussed.

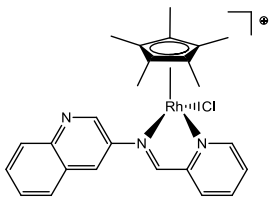

Figure 1: The metal complex used in this study [Rh (η^5-Cp^*)Cl(quinpy)]Cl (quinpy = (E)-1-(pyridin-2-yl)-N-(quinolin-3-yl)methanimine).

The financial support of Obra Social "la Caixa" (project OSLC-2012-007), MINECO (CTQ2014-58812-C2-2-R, FEDER Funds) and Junta de Castilla y León (BU042U16, FEDER Funds), Sapin is gratefully acknowledged

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Assemblea Ordinaria dei Soci del Gruppo Giovani

Mercoledì 26 Ottobre 2016 – h 18.50

Ordine del giorno

1. Comunicazioni
2. Relazione annuale del Consiglio Direttivo
3. Consuntivo amministrativo e preventivi di spesa
4. Proposta di modifica delle attività di spoglio relative all'elezione del Consiglio Direttivo del Gruppo Giovani
5. Proposta di accorpamento delle figure "Socio Giovane" e "Socio Junior"
6. Programmazione delle attività future del Gruppo Giovani
7. Varie ed eventuali

European Young Chemists' Network

SCI Young members are invited to follow the activities of the European Young Chemists' Network (**EYCN**), i.e. the young group of the European Association for Chemical and Molecular Sciences (**EuCheMS**), that brings together chemistry-related organisations throughout Europe to provide a single voice on key science and policy issues, based on expert scientific knowledge.

In this Merck Young Chemists Symposium we host Camille Oger, board member of EYCN, who will show you the activities of EYCN (events, conferences, prizes, etc.). You are invited to like the Facebook webpage of EYCN:

facebook EYCN

EYCN will also award two posters presented during this conference!

National delegates at the 11th Delegates Assembly in Guimarães (April 2016).

SCI thanks EYCN and its main sponsor Evonik Industries for their financial support within this conference

EVONIK INDUSTRIES

EYCN: 10 years connecting European young chemists

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The European Young Chemists' Network (EYCN) is the younger members' division of EuCheMS. It was created back in 2006 and has grown to represent 26 different societies from 22 European countries [1].

The EYCN organizes different activities throughout Europe: several poster prizes in younger chemists' conferences; the European Young Chemist Award (EYCA) [2]; career days for young students; and since 2011, the Young Chemists Crossing Borders exchange programs in collaboration with the Younger Chemists Committee of the American Chemical Society [3].

In April 2016, EYCN hosted the first European Young Chemists' Conference in Guimarães, Portugal, and others are coming. EYCN also participated in the activities of EuCheMS Congress in Seville 2016 and gave young chemists around Europe a unique opportunity to meet, create new connections and develop their soft-skills thanks to the training courses and seminars.

If you wish to get in touch with the EYCN, visit our website (http://www.eycn.eu) or contact us using our social media profiles in Facebook, Twitter and LinkedIn. We look forward to collaborating with you!

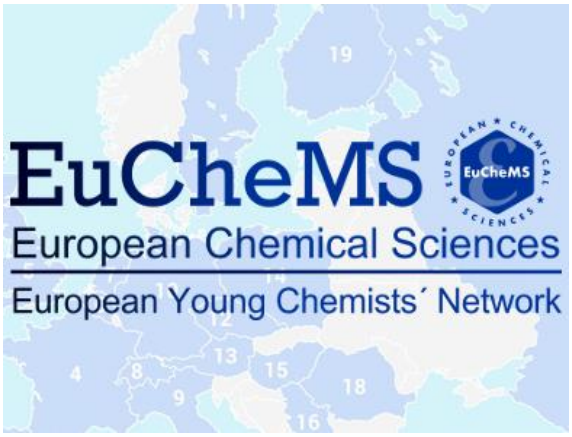

Figure 1: EYCN logo.

[1] F. Gomollón-Bel, C. Oger and C. Todasca. *Chem. Views*, DOI: 10.1002/chemv.201500500.
[2] The EYCA Award is organized in collaboration with the Italian Chemical Society and the Italian Consiglio Nazionale dei Chimici.
[3] U. I. Zakai, N. LaFranzo, C. Dunne and J. Breffke. *Chem. Views*, DOI: 10.1002/chemv.201500051.

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