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BOOK OF ABSTRACTS

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XVIII edition

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Welcome message

Dear participants,
welcome to the 18th edition of the **Merck & Elsevier Young Chemists Symposium**, formerly SAYCS and MYCS.

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

This symposium is fully devoted **to young researchers**, such as MSc and PhD students, post-doc fellows and young researchers in companies. 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 **chemistry from knowledge to innovation**: *how chemistry is increasingly present in all of the fields that are essential for human life, and how chemical fundamentals are pushing novel technologies?*

This year we have the exceptional number of 212 participants; we thank you for the great trust shown towards SCI Giovani, Merck and Elsevier.

Enjoy the conference!

Federico Bella
Coordinator of SCI-Giovani

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

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PL-1

Self-organization and emerging properties of halogenated peptide assemblies

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A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.[1] Although many modifications of amyloidogenic sequences have been utilized to tune their self-assembly behavior, halogenation has rarely been pursued. The advantage of a strategy based on the introduction of halogen atoms on peptide motifs lies in the fact that halogenation is a minimal structural modification, which, on the other hand, may induce a large difference in the peptide supramolecular behavior as a consequence of the rich variety of noncovalent interactions given by halogen atoms.

In this presentation, I will show how the halogen bond can be used to promote the molecular self-assembly of peptides. We have applied this new supramolecular concept to the augmented fibrillation of amyloidogenic peptides[2,3] and the control of their nanostructures[4] (Figure 1). The obtainment of a novel unnatural amino acid functioning as strong halogen-bond donor has allowed to engineer the hydrophobic cavity of an amyloid fibril. Implications in molecular mechanisms of diseases and examples of novel biomimetic elastomers will also be presented.

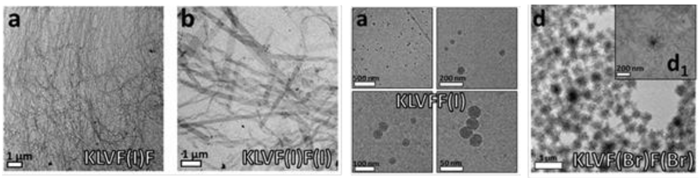

Figure 1. Halogenated derivatives of KLVFF showing various nanoarchitectures.

[1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **116** (2016) 2478-2601.
[2] A. Bertolani, A. Pizzi, L. Pirrie, L. Gazzera, G. Morra, M. Meli, G. Colombo, A. Genoni, G. Cavallo, G. Terraneo, P. Metrangolo, *Chem. Eur. J.* **22** (2017) 2051-2058.
[3] A. Bertolani, L. Pirrie, L. Stefan, N. Houbenov, J.S. Haataja, L. Catalano, G. Terraneo, G. Giancane, L. Valli, R. Milani, O. Ikkala, G. Resnati, P. Metrangolo, *Nat. Commun.* **6** (2015) art. no. 7574.
[4] A. Pizzi, L. Lascialfari, N. Demitri, A. Bertolani, D. Maiolo, E. Carretti, P. Metrangolo, *CrystEngComm* **19** (2017) 1870-1874.
[5] A. Pizzi, C. Pigliacelli, A. Gori, Nonappa, O. Ikkala, N. Demitri, G. Terraneo, V. Castelletto, I.W. Hamley, F. Baldelli Bombellia, P. Metrangolo, *Nanoscale* **9** (2017) 9805-9810.

Acknowledgements: The ERC, projects no.s 307108 and 789815, and Fondazione Cariplo, project 2014-0746, are gratefully acknowledged for funding.

PL-2

Single molecule detection of markers with a label-free bio-electronic sensor

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Label-free single-molecule detection has been achieved so far by funnelling a large number of ligands into a sequence of single-binding events with few recognition elements host on nanometric transducers. Such approaches are inherently unable to sense a cue in a bulk milieu. Conceptualizing cells' ability to sense at the physical limit by means of highly-packed recognition elements, a millimetric sized field-effect-transistor is used to detect a single molecule. To this end, the gate is bio-functionalized with a self-assembled-monolayer of trillions of capturing anti-Immunoglobulin-G and is endowed with a hydrogen-bonding network enabling cooperative-interactions. The selective and label-free single-molecule IgG detection is strikingly demonstrated in diluted saliva while 15 IgGs are assayed in whole serum. The suggested sensing mechanism triggered by the affinity binding event, involves a work-function change that is assumed to propagate in the gating-field through the electrostatic hydrogen-bonding network. The proposed immunoassay platform is general and can revolutionize the current approach to protein detection [1].

[1] E. Macchia, K. Manoli, B. Holzer, C. Di Franco, M. Ghittorelli, F. Torricelli, D. Alberga, G.F. Mangiatordi, G. Palazzo, G. Scamarcio, L. Torsi, *Nat. Commun.* **9** (2018) art. no. 3223.

PL-3

Addressing renewable energy challenges with quantum chemistry

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Global advances in industrialization are precipitating the rapid consumption of fossil fuel resources with increasing levels of atmospheric greenhouse gases. After the UN international conference on climate change (Paris 2015) and despite the recent political shift in USA, there is a worldwide consensus on implementing all possible actions to dislodge our dependence on oil, coal and natural gas. World sustainability requires viable sources of renewable energy and new technologies for its efficient conversion into commodities such as fuels or electricity.

Chemistry and materials sciences play a pivotal role in optimizing the functional materials that are at the core of energy conversion devices. This is not a trivial task. The conversion of energy is the result of several physical and chemical processes that involve chemical reactions, charge and mass transport occurring across multiple heterogeneous interfaces. Often, experimental techniques cannot dissect subtle features at the nanoscale that can hinder an effective design of new devices. Thus, the application of computational modeling tools with atomistic resolution represents an ongoing revolution in materials design and device development.

In this context, Quantum Mechanics (QM) offers an unbiased guide for characterizing the complex materials properties and predicting the key processes at the atomic scale. In particular, I will review our recent QM studies of electrode materials for energy conversion devices, from dye-sensitized solar cells [1] to solid oxide electrochemical cells [2,3]. These results will highlight the merits of Density Functional Theory for gaining qualitative insights on important materials properties. At the same time, we will discuss the limits of current standard approaches for complex reactions at heterogeneous interfaces, as for example the oxygen reduction reaction at electrode surfaces. A viable multi-scale scheme based on density functional embedding theory can solve these problems and can provide predictions in quantitative agreements with experiments [4]. Future directions for the application of quantum chemistry to renewable energy technologies will be outlined.

[1] A.B. Muñoz-García, M. Pavone, *Phys. Chem. Chem. Phys.* **17** (2015) 12238-12246.
[2] M. Pavone, A.M. Ritzmann, E.A. Carter, *Energy Environ. Sci.* **4** (2011) 4933-4937.
[3] A. Muñoz-García, M. Tuccillo, M. Pavone, *J. Mater. Chem. A* **5** (2017) 11825-11833.
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INV-1

Come to chemometrics: we have cookies (and whisky, and beer)

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The story so far: in 1974 Chemometrics was created [1]. This has made a lot of people very angry and been widely regarded as a bad move [2].

But don't panic. The final aim of this talk is to demonstrate that, after all, developing such a thing as Chemometrics was not at all a bad idea.

It all started from the need of tackling and solving typical problems in analytical chemistry, like determining the number of components in a spectrum of mixtures [3]. Lots of efforts and resources were put in organizing and performing the experiments but obtaining information from the resulting data was (is!) usually a difficult and time-consuming task.

With the aim of extracting information from data and visualizing it in an accessible way, a wide range of chemometric tools have been developed since and nowadays the most established methods are becoming more and more popular in fields other than Chemistry or Food Science.

This talk is intended to give an overview of what Chemometrics is in practice, using real cases that I have encountered during my experience as a PhD Student in Chemometrics.

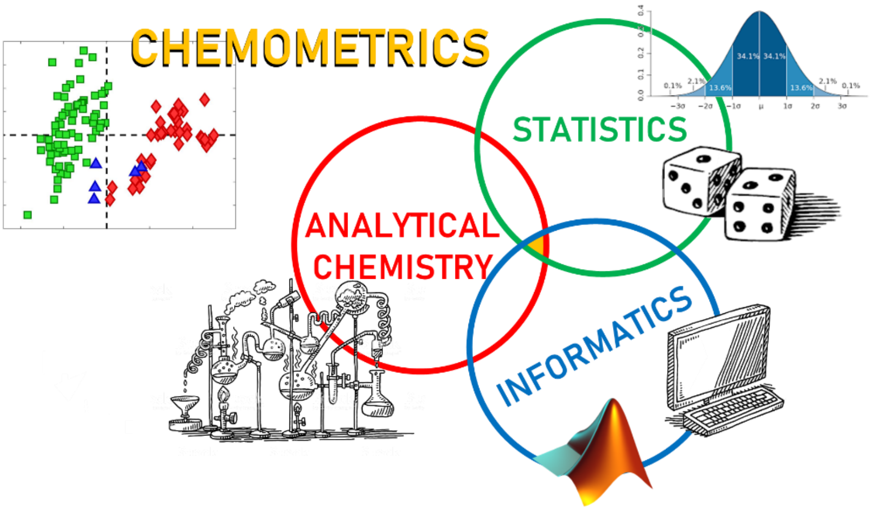

Figure 1: Chemometrics: a simple overview.

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[2] N.A. Douglas, *The Restaurant at the End of the Universe*, Pan Books, 1980.
[3] R.G. Brereton, J. Jansen, J. Lopes, F. Marini, A. Pomerantsev, O. Rodionova, J.M. Roger, B. Walczak, R. Tauler, *Anal. Bioanal. Chem.* **409** (2017) 5891-5899.

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OR-1

Novel sustainable processes and materials for polymer electrolytes in sodium-ion batteries

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In recent years, large-scale energy storage systems are becoming extremely important to realize the load levelling of intermittent renewable energy sources, such as wind and solar, into the grid. Secondary (rechargeable) sodium-based batteries may represent the key enabling technology in this respect, because of high-energy density, low-cost, simple design, and easiness in maintenance. However, currently studied materials and processes are not in line with a truly sustainable point of view.

Here, we offer an overview of our recent developments on innovative polymer electrolytes for sodium-ion batteries. In our labs, we develop different kind of polymer electrolytes by means of different techniques, including simple solvent casting [1] and UV-induced photopolymerization (UV-curing) [2,3], being simple, low-cost and easily scalable to an industrial level. Besides, our research focuses on new sustainable polymers such as cellulose or linear polyglycidols, that could be a solution in future applications. All samples were thoroughly characterized from the physico-chemical and electrochemical viewpoints. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation even at ambient conditions. Electrochemical performances in lab-scale devices were evaluated by means of cyclic voltammetry and galvanostatic charge/ discharge cycling exploiting different electrode materials.

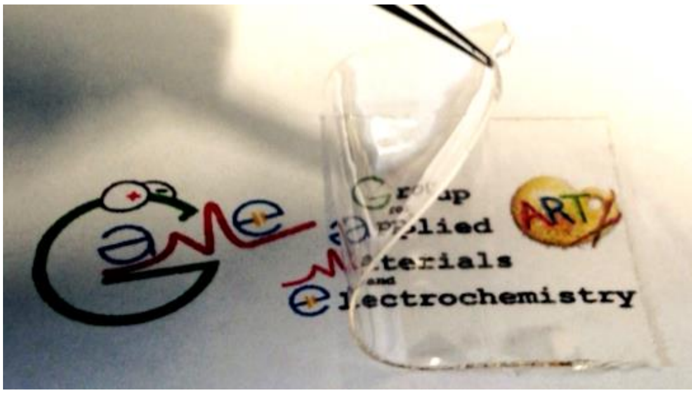

Figure 1. Digital photograph of a UV-crosslinked methacrylic-based polymer electrolyte membrane.

[1] F. Colò, F. Bella, J.R. Nair, M. Destro, C. Gerbaldi, *Electrochim. Acta* **174** (2015) 185-190.
[2] F. Bella, F. Colò, J.R. Nair, C. Gerbaldi, *ChemSusChem* **8** (2015) 3668-3676.
[3] F. Colò, F. Bella, J.R. Nair, C. Gerbaldi, *Electrochim. Acta* **365** (2017) 293-302.

OR-2

What is the driving force for collagen protein folding? Insights from hybrid DFT simulations

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Collagen is one of the most abundant protein in mammals. It is the building block of complex hierarchical structures such as bones and tendons [1]. Its structural peculiarity is the geometrical motif in which three parallel polypeptides strands coil about each other to form a triple helix (see Figure 1) [1]. The primary structure of collagen is mainly restricted to a triplet repeated sequence, which occurs in all types of collagens [2]. In each triplet, glycine (Gly) always occupies the first position, while proline (Pro) and its derivatives, e.g. hydroxyl-proline (Hyp), are the most common amino acids in the second and the third positions, respectively. Within all collagens, Gly appears most frequently (33%), and Pro and Hyp represent the ~22% of all residues [3]. Hyp is not directly incorporated in the protein. Indeed, the process of hydroxylation of the Pro ring occur after collagen formation in cells. It has the relevant role of increasing the stability of the collagen preventing rapid denaturation at human body temperature. In the last decade, several experimental studies were carried out to explain energetic reasons of this stabilization effect. Despite the large amount of work done, the scenario is still not clear.

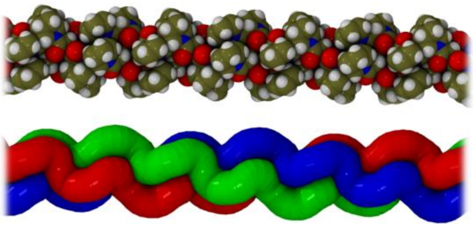

Figure 1. Collagen protein.

Molecular simulation at the DFT level combine atomic resolution and chemical accuracy, and can be an useful tool for investigating biological systems. Its main limitation is the size of the systems investigable, which is very limited, so it is a method rarely employed in protein science. Thanks to highly symmetrical collagen models, we reduced the computational cost of our calculations, thus succeeding to compute the folding process of collagen triple helix. Moreover, we focused on the role of the Pro hydroxylation comparing the folding energy for hydroxylated and non-hydroxylated Collagens. Water molecules, which have a very delicate role in the folding process, must be included explicitly in the simulations for a reliable representation of this natural phenomenon.

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OR-3

Transfer hydrogenolysis of benzyl phenyl ether promoted by the bimetallic Pd/Co catalyst

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One of the major challenges in the catalytic valorization of lignin is the selective cleavage of the C–O bond [1]. Therefore, in order to develop selective catalytic processes for the production of aromatics from lignin, a complete understanding of the molecular aspects of the basic chemistry and reactivity of aromatic ethers is still crucial. A lot of research affords have been directed to the study of the catalytic hydrogenolysis of benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and diphenyl ether (DPE) that are the simplest model molecules of α-O-4, β-O-4 and 4-O-5 lignin linkages.

CTH reactions has recently gained increased attention as an efficient alternative to the direct use of molecular hydrogen by improving the sustainability and economics of hydrogenation reactions [2,3].

In this context, to further explore the enhancement of the palladium activity promoted by other transition metals, the Pd/Co bimetallic catalyst was prepared by using the coprecipitation method and fully characterized by TEM, XRD, H_2-TPR, XPS and EXAFS.

By using Pd/Co as the catalyst and 2-propanol as the H- source, under batch conditions, an appreciable BPE (0.1 M) conversion was achieved after 90 minutes at 210 °C. The conversion of BPE increased by increasing the reaction temperature and it was fully converted at 240 °C. Transfer hydrogenolysis reactions over 2-phenethylphenylether (PPE) and diphenyl ether (DPE) were also investigated. Catalytic tests show that the cleavage of C-O bond of PPE and DPE is less efficient due to the higher bond dissociation energies (β-O-4 = 289 kJ/mol and 4-O-5 = 314 kJ/mol) involved.

Reactions carried out with the analogous Pd/Co catalysts prepared by using the impregnation method are by far less efficient. Therefore, the enhanced catalytic performance shown by Pd/Co catalyst can be related to the coprecipitation method that allows the formation of bimetallic PdCo ensembles that positively promote the C-O bond cleavage of aromatic ethers.

[1] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **114** (2014) 1827-1870.
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[3] M. J. Gilkey, B. Xu, *ACS Catal.* **6** (2016) 1420-1436.

OR-4

Cellulose functionalization: comparison between wet-chemistry hydrophobization vs. photopolymerization

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In this study, cellulose has been functionalized with two different methods. In the first one, cellulose fibers are chemically functionalized by introducing palmitate groups under mild condition in order to confer hydrophobic properties. The effectiveness of the functionalization has been evaluated by FTIR spectroscopy and thermo-gravimetric analyses (TGA), whereas the structural integrity has been confirmed by XRD measurements. The prepared materials have been tested in water remediation processes as sorbing materials and using fatty oils mixtures from both animal (cod liver oil) and vegetable (sunflower oil) sources as target substrates. Kinetic measurements evidenced that the best performances were reached toward the sunflower oil, pointing out the promising application of such green materials as a sustainable alternative tools for oil-water remediation processes [1]. In the second process, photo-polymerization is presentedas an alternative method of functionalization widely exploited in many technological fields, due to its high versatility and fast reaction rates. For this purpose, poly(ethylene glycol) methacrylate (PEGMA) nanostructures were grown onto cellulose following a simple and promising light-driven reaction mechanism involving benzophenone (as photo-initiator) and UV-curing. The effectiveness of the surface functionalization has been determined by means of morphological and physicochemical characterizations, showing the formation of very sharp PEGMA nanometric architectures [2].

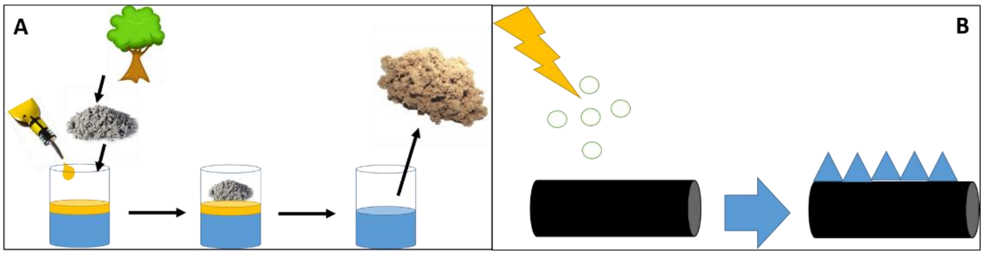

Figure 1. A) Palmitate cellulose as an absorbent materials; B) Photo-induced polymerization of PEGMA nanoarchitectures.

[1] L. Lavagna, R. Nisticò, S. Musso, M. Pavese, *Wood Sci. Tecnol.* (under evaluation)
[2] L. Lavagna, R. Nisticò, A. Chiappone, M. Pavese, *Mater. Lett.* **227** (2018) 202-204.

OR-5

On the toluene adsorption on hyper cross-linked polymers

Federico Begni, Giorgio Gatti, Chiara Bisio, Geo Paul, Diana F. Olivas Olivera, and Leonardo Marchese

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Pollutants removal from the environment has proven to be difficult and expensive. In order to address this problem, various methods for the removal of organic contaminants have been developed in recent years such as oxidation, reverse osmosis, ion exchange, etc. [1]. In this respect, adsorption is considered a very promising alternative due to its universal applicability, ease of operation and cost effectiveness. Hence, a growing number of porous sorbents have been developed, ranging from completely inorganic frameworks, such as zeolites, to entirely organic structures like porous polymers. In this work, we studied and compared the adsorption capacities of toluene on different materials including well established adsorbents, such as zeolites and mesoporous silica and novel materials, such as hyper cross-linked polymers (HCPs). HCPs were prepared as reported in the literature and using different ratios between monomer tetraphenylmethane (TPM) and cross – linker, formaldehyde dimethyl acetal (FDA) [2]. Synthetic route for HCPs consists of employing a Friedel – Crafts alkylation using $FeCl_3$ as catalyst to promote the formation of a rigid, highly cross-linked framework. By using different TPM/FDA ratio materials with a different degree of cross-linking can be obtained. Adsorption data showed a higher toluene uptake for HCPs with respect to zeolites and silicas (in particular, Y and MCM-41 solids). In order to gain insights into the nature of host-guest interactions we performed adsorption of fully deuterated toluene on HCPs, monitoring the process through FT-IR and SS-NMR spectroscopy. By combining volumetric analysis and spectroscopy methods it was derived that the organic nature of the aromatic framework displayed by HCPs together with their high surface area are key properties to improve significantly the toluene adsorption capacities.

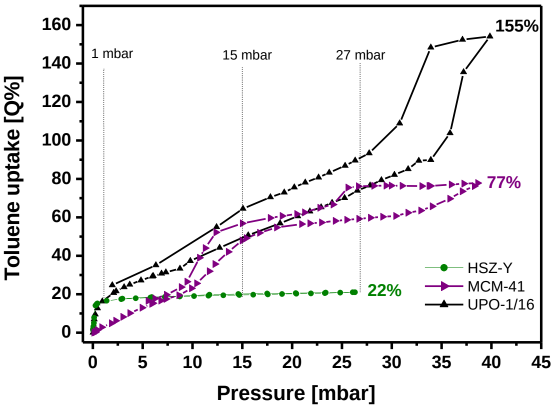

Figure 1. Adsorption isotherms of toluene adsorbed on HCP UPO-1/16 compared with Zeolite Y and silica MCM-41.

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OR-6

PGSE NMR studies on complex formulation of aminoacid deriving polymers and sodium deoxycholate micelle

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The design of chiral synthetic polymers capable of self-assembling in solutions is receiving increasing attention for its biological implications. In this field, polyamidoamino acids (PAACs) are an emerging class of stimuli-responsive bioinspired synthetic polymers obtained by the stepwise polyaddition in pH > 9 aqueous solution of α-amino acids with N,N′-methylenebisacrylamide. The first example of this family, ARGO7, obtained from L- and D-arginine polyaddition, proved capable of self-assembly in aqueous solution into rigid pH dependent conformations [1]. For all ARGO7 isomers, self-diffusion coefficients probed by pulsed-gradient spin-echo nuclear magnetic resonance (PGSE-NMR) reported values between 3×10^{-10} and 9×10^{-11} m^2/s and R_h of 0.9 - 2 nm, consistent with compact random coils. It remains to be ascertained if selective chirality driven interactions may arise by mixing the D- or L- form of PAACs with soft chiral surfaces. As an example of the latter, sodium deoxycholate was chosen for its ability to form chiral micelle in aqueous solution, capable of interacting with protein and fatty acids in biological system [2].

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OR-7

Silica coated hemp fabrics and microfibers through a green ecofriendly chemical approach

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Through a new and ecofriendly chemical approach, using inexpensive waterglass solutions, a silica-based coating was promoted on hemp fabrics which allows, also, to obtain silica coated micro-hemp particles, with an average aspect ratio of 7.1 (see Fig. 1), from rags. This green coating is able: (i) to act as a thermal shield [1], (ii) to tailor the surface with specific coupling agents for suitable polymer matrices.

The study was performed with the aid of multiple investigation techniques: Fourier-Transform InfraRed Spectroscopy, FTIR, Scanning Electron Microscopy, SEM, X-Ray powder Diffraction, XRD.

The fire behavior, that, owing to severe regulations (i.e., in aerospace engineering), often prevents composites applications, was also studied. Cone calorimetry and vertical burning tests showed a considerable improvement in terms of fire behavior in the case of silica coated fiber reinforced polymer composites.

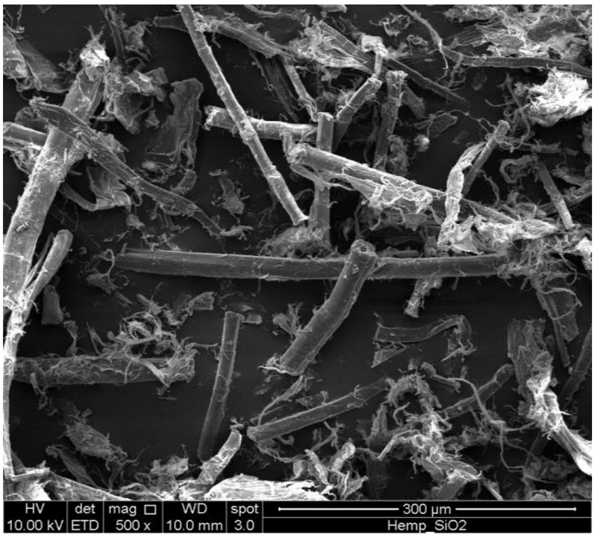

Figure 1. Overall production process scheme for micro-hemp particles.

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OR-8

Chemistry and friction: a new method to investigate tribological problems

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Carbon materials are the most widely used solid lubricants in the formulation of composite for frictional applications, as brake pads. In this field, their main role is to reduce and stabilize the friction coefficient during brake. This property derives from their structure, constituted by strong bonding within the basal planes and weak bonding between them, which allows the formation of a lubricant layer that ensures a stable friction.

Although this mechanism has been extensively studied [1], each carbon material has its own tribological behaviour and the reason of these differences is still unknown. With the aim to set up a characterization method devoted to disentangle the differences in friction properties, the authors focus the attention on a system of seven carbon materials.

The composition, morphology, density and structure of four graphite and three coke materials were investigated to the purpose for correlating the chemico-physical properties with the friction behaviour. The morphological properties were evaluated by optical and electron scanning microscopy (OM and SEM), while density was measured by helium pycnometer. The structural features were investigated using X-ray diffraction and Raman spectroscopy.

Due to the multivariate nature of friction behaviour, the obtained data were analysed using the Peason coefficient and the chemometrical approach. The first allows to find significant correlations between friction coefficient and the parameters obtained by chemico-physical characterization. The second method shows how each variable affects friction in function of the influence of all the other parameters at the same time.

The method applied allows to understand the differences of carbon materials friction and represents an important task to disentangle the complexity of tribological phenomena occurring at interface.

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OR-9

Alkyl carbonates as non-toxic reagents for selective gas-phase alkylation of phenolics

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Alkyl carbonates are biodegradable and non-toxic compounds widely used as aprotic polar solvents and obtainable from CO_2 [1]. They are considered a greener alternative to many hazardous chemical intermediates (e.g. methyl iodide and dimethyl sulfate). Over basic catalysts, carbonates are much more reactive than their parent alcohols as alkylating reagents of soft nucleophiles (e.g. phenol), with a chemo-selectivity strongly directed toward oxygen alkylation [2]; this behavior was confirmed by reacting phenol with diethylcarbonate (DEC) over magnesium oxide obtaining ethylphenyl ether with 70% selectivity at relatively low temperature (350°C). In order to increase the versatility of this approach, the present research focused on the development of bifunctional Mg/Al/O catalyst (possessing both acidic and basic properties) capable to drive the chemo-selectivity from O-alkylated to C-alkylated products. At low temperatures basic sites only are active and are responsible of O-ethylation; rising reaction temperatures leads to O-ethylation on basic sites together with isomerization of ethyl phenyl ethers on acidic Al-sites. This cascade effect directs the overall chemo-selectivity to C-alkylated products and the overall regio-selectivity towards ortho-isomers, even if a minor contribute of direct C-alkylation cannot be excluded. Therefore, the modulation of catalyst basicity obtained replacing part of Mg^{2+} ions with Al^{3+} ions resulted in a catalyst which allows the use of biodegradable and non-toxic alkyl carbonates for both C-alkylated and O-alkylated phenolics production as a function of reaction temperature.

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OR-10

Multiwalled carbon nanotubes: chemical physical characterization and rheological effect on bitumen

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Currently the growth in road traffic and the load to which they are subjected the road surface together with the adverse environmental condition leads to rapid deterioration of pavements. In order to increase the performance of asphalt and to increase the life time, a new generation of blend asphaltic is required.

Since the first discovery in 1991 [1] multi-walled carbon nanotubes (CNTs) have attracted enormous research attention in various scientific communities. Indeed CNTs have amazing properties including high Young's modulus, good tensile stability, high thermal conductivity, high surface density [2]. A CNTs is a one-atom thick sheet of graphite rolled up into a seamless hollow cylinder with a diameter of the order of one nanometer [3].

This study is based on the role of multi-walled carbon nanotubes (CNTs) on the bitumen structure and their use as bitumen modifier. Two different types of CNTs were tested: one characterized by high purity and another one characterized by some surface defects. Difference of microstructure of multi-walled carbon nanotubes and the rheological behavior of modified bitumen were investigated. The defects of multi-walled carbon nanotubes seem to anchor the asphaltenes in the bitumen forming a stable network and shifting (higher temperature) the phase transition from viscoelastic to liquid phase.

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OR-11

An integrated and versatile biorefinery model to produce lipids from second generation biomass

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In order to replace fossil fuels and products with biofuels and bioproducts, and, at the same time, to avoid the competition food versus fuel related to renewable resources, innovative processes aimed to valorize lignocellulosic biomass and agro-food waste as raw material are highly attractive.

Arundo donax L. or giant reed was defined as a promising lignocellulosic crop in the biorefinery field for several reasons: no food competition, high yield (30 tons/ha/yr), high structural carbohydrate content (55-60%), low price (15€/ton), low input management system, ability to grow in marginal and polluted soils, and applications in phytoremediation process [1].

The present study focused on investigating innovative, tailored and integrated strategies to firstly produce glucose and xylose from *A. donax*, by using green catalysts and microwaves as heating system, and then on fermenting them into fatty acid methyl esters (FAMEs) by oleaginous yeasts *Lypomyces starkeyi* and *Cryptococcus curvatus* [2]. Moreover, glycerol deriving from FAMEs production was recycle as a fermentative substrate according to a zero waste biorefinery scheme.

The quantitative conversion of hemicellulose into xylose was performed by optimizing both homogeneous ($FeCl_3$ 1.6% w/w, 150 °C, 2.5 min; H_2SO_4 0.2% w/w, 170 °C, 2.5 min) and heterogeneous (Amberlyst70 20% w/w biomass, 160 °C, 20 min) catalysis. The cellulose remained in the solid residue recovered at the end of the first step was then hydrolyzed by testing dilute H_2SO_4 (0.2% w/w, 190 °C, 5 min) or the enzymatic mixture Ctec2 (15 FPU/g glucan, 50 °C, 72 h), obtaining an overall yield of about 40-50% g glucose/ g glucan for both approaches.

The FAMEs profile contained palmitic, oleic and linoleic acids proving the possibility of using microbial lipids as an efficient alternative to vegetable oils to produce biodiesel, bioplastics, biosurfactants and animal feed.

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OR-12

Kinetic study of the levulinic acid esterification with ethanol promoted by Amberlyst-15

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Levulinic acid (LA) was recognized by the U.S. Department of Energy as one of the top biomass-derived platform molecules, due to its high reactivity and for its low-cost production from lignocellulose wastes. Levulinic acid esters may find applications as alternative green solvents, polymer plasticizers and fragrances [1]. LA esterification with alcohols is an acid catalyzed reaction, promoted by homogeneous catalysts (i.e. sulfuric acid [2]); since recent times a variety of heterogeneous acid catalysts have been used (i.e. zeolites, sulfated metal oxides, silica, sulfonated resins) [2,3]. Amberlyst-15 showed a remarkable high yield to ethyl levulinate, due to the acidity provided by sulfonic groups. In the present work, the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15 was investigated. Experiments were conducted by evaluating the effect of different operating conditions on the reaction rate (i.e. stirring rate, temperature, catalyst loading and reactants ratio). Through this study it was possible to evaluate the activation energy value (49.39 kJ/mol). The collected experimental data were interpreted with a reliable model taking into account also for the mass transfer phenomena involved in the reaction network, such as eventual fluid-solid and intraparticle mass-transfer limitations. The mixed PDE/ODE system (Eq.1) given by the mass balance equations, was solved with advanced numerical techniques.

$$\frac{\partial C_{i,s}}{\partial t} = \frac{D_{eff,i}}{\varepsilon \cdot x^s} \cdot \frac{\partial}{\partial x}\left(x^s \cdot \frac{\partial C_{i,s}}{\partial x}\right) + \sum_{k=1}^{N} \frac{\rho}{\varepsilon} \cdot r_k \tag{1}$$

The results can be considered as good starting point for continuous reactors optimization.

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OR-13

Advances in CO_2 capture by task specific bio-based ionic liquids

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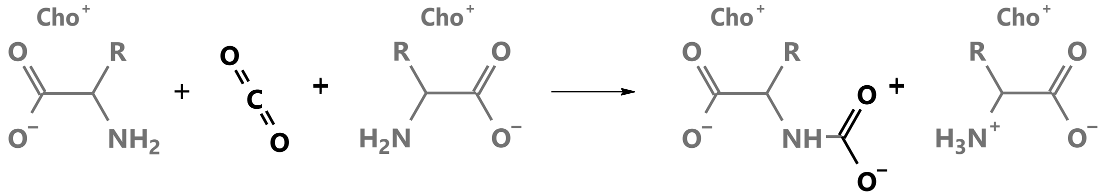
Opposing global warming due to greenhouse effect is a key challenge that humankind is called to face in the next years. Carbon dioxide excess is one of the main causes of such temperature increase, thus reducing its emission in the atmosphere through capture and/or utilization is a valuable strategy to limit greenhouse effect. Presently, aqueous amine solutions is the applied technology for CO_2 sequestration, but, due to the energy intensive release step, toxicity and corrosiveness, amine scrubbing could not represent a long-term solution in CO_2 capture. Ionic liquids (ILs), organic salts in the liquid state near room temperature, are a class of emerging materials with a great potential towards CO_2 capture [1]. Recently the combination of the choline cation with amino acids (AAs) based anions gave rise to a wide set of bio-inspired ILs with low toxicity [2], that are optimal candidates for CO_2 capture. Physico-chemical properties of these ILs have been extensively studied but few studies have been conducted on the CO_2 absorption [3]. In this work, CO_2 absorption on eight different AA-ILs were studied testing four AAs and two different cations. For the first time, the synthesis of ILs based on acetylcholine is reported. CO_2 absorption capacities in solution and other properties of these ILs were measured. In addition, a new *operando* IR spectroscopic setup was employed to monitor the CO_2-IL reactivity, allowing the disclosure of the reaction mechanism.



Scheme 1. CO_2 absorption reaction on amino acids based ionic liquid.

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OR-14

Intensification of calcium carbonate precipitation in a packed bed reactor

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INTRODUCTION: Calcium Carbonate micro and nanoparticles (CCnP) are widely synthesized via carbonation route [1], and are recently being evaluated as potential cement and polymer fillers [2]. The aim of this study is performing the carbonation process to produce CCnP to be used as filler in the cement.

METHODOLOGY: Stirred Tank (STR) and Packed Bed Reactor (PBR) were studied in order to tailor the properties of the final product. The studies were carried out employing Calcium Oxide suspension at different concentrations (0.015-0.05 M) until pH reached 10, below which precipitation becomes negligible due to bicarbonate prevalence. In the STR the gas was fed at the bottom of the reactor, which was under constant agitation. On the other hand, the vertical PBR, both liquid and gas were fed from the bottom of the reactor, and the product was recycled to the original suspension. The synthesized particles were subsequently filtered by vacuum, repeatedly washed and dried at 90 °C and it was ready for characterization.

RESULTS HIGHLIGHTS: Higher Ca^{2+} Concentrations leaded to the synthesis of larger particles owing to growth and agglomeration phenomena. By increasing the CO_2 flow rate, the synthesis time was reduced, which lead to smaller particles formation. Nevertheless, STR presents micromixing issues, which leads to the formation of microsized particles with high polydispersity. The PBR enhances the mass transfer owing to the formation of a thin film over the packing, were micromixing is favoured. Since many factors such as, supersaturation degree, synthesis time, flowrates and the film thickness above the packing may affect the particle size, optimal operating conditions were determined, thus synthesizing particles with a volume average size of 400 nm as seen in Figure 1.

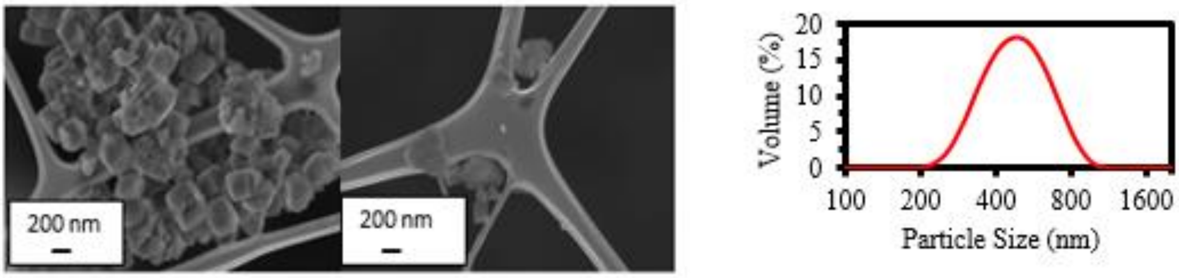

Figure 1. Morphology and size characterization of the $CaCO_3$ particles synthesized at optimal operating conditions with the PBR.

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OR-15

Copper (0) nanoparticles in glycerol: an efficient and versatile catalyst for hydride-free reduction of nitro derivatives

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Due to their importance in the chemical and pharmaceutical industries, many synthetic routes have been reported for the catalytic reduction of aromatic nitrocompounds to the corresponding aryl amines. However, these systems normally operate under strong and risky conditions and involve the utilization of hazardous reducing agents such as H_2, $NaBH_4$, formic acid or hydrazine hydrate. Thus, simple, environmentally friendly, highly efficently and inexpensive alternatives are needed.

Herein, we report an efficient and hydride free method for the chemo selective reduction of aromatic nitro compounds catalyzed by Cu nanoparticles. Aiming to carry out the reaction lowering the energy and time consumption, enabling technologies such as microwaves and ultrasounds have been applied. In addition, bio-glycerol has been employed as hydrogen source, making the process attractive in terms of ease of handling, non-toxic nature and environmental perspectives.

The new technique allowed to selectively synthesize azoderivatives as well as fully reduced amino compounds. Specifically, nitrocompounds were reduced to anilines operating at high temperature, while corresponding azoderivatives were synthesized operating at lower temperature. A wide range of anilines with different substituents and symmetric azocompounds was obtained in a single reduction step, with excellent yields and in a very short reaction time.

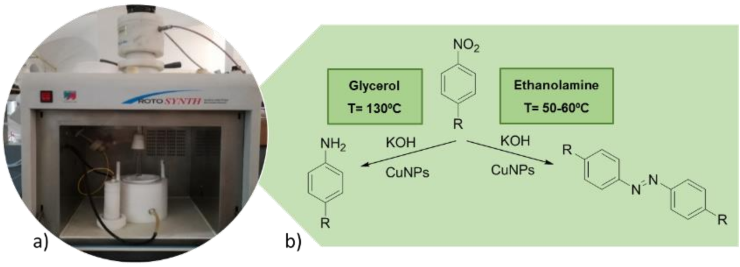

Figure 1. a) Combined MW/US device. b) Selective reduction of aromatic nitrocompounds.

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OR-16

Structure-effects correlation on symmetry breaking phenomenon in supramolecular aggregates of porphyrin based polymers

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The spontaneous symmetry breaking is a controversial natural phenomenon that occurs in every scientific field, from nuclear physics to biology. In chemistry, this phenomenon is investigated by studying achiral molecules' supramolecular aggregates. It was already used a particular achiral star-polymer based on a porphyrin derivative that shows spontaneous aggregation in water solution, the 5,10,15,20-tetrakis[p-(ω-methoxy-polyethyleneoxy)phenil]porphyrin (Star350) [1]. It was already demonstrated that the symmetry breaking phenomenon in supramolecular aggregates of Star350 can be induced and annulled by the interaction with asymmetrical thermophoretic forces [2]. It is possible to manage the phenomenon not only in magnitude but also in enantiomeric enrichment, just acting on the direction and the intensity of the asymmetrical weak thermal gradient applied to the stagnant solution [3]. We studied the effects of the building blocks' structure on the symmetry breaking phenomenon. We used some PEGylate porphyrin derivatives isobars to the Star350, but with different molecular arrangements: a transoid one [the 5,15-[p-(ω-methoxy-polyethyleneoxy)phenil]-10,20-di[p-hydroxyphenyl]porphyrin (Trans750)], and a cisoid one [the 5,10-[p-(ω-methoxy-polyethyleneoxy) phenil]-15-20-di[p-hydroxyphenyl] porphyrin (Cis750)]. We also used a cyclic dimer of the Cis750 (Di-Cis750), having a star-like molecular arrangement similar to the Star350 system, but with a higher hydrophobic core. For every building block we studied the quali-quantitative differences with respect to the aggregation phenomenon, by UV-visible and circular dichroism spectroscopies. Thanks to the circular dichroism experiments, conducted in thermal ramp and in stagnant water solution, was found a probable cause-effect correlation between the molecular arrangements of the building blocks and the symmetry breaking phenomenon. In particular, the roles of the supramolecular aggregates' intermolecular forces and of the aggregates' mesoscopic morphology have been taken into consideration.

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OR-17

Interface dynamics at oscillating air bubbles

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Fluid interfaces exhibit markedly different behaviour with respect to bulk phases, resulting from the supramolecular assembly of interfacial molecules (bidimensional monolayers). While the static properties of such aggregates are widely acknowledged, less is known about their dynamics. An example is given by capillary waves (ripples) at the surface of oscillating bubbles or drops, whose distinctive features depend on the chemical composition of the interface (affecting charge, viscosity and surface tension).

We have studied oscillating interfaces by means of a bubble (drop) model system (as in Figure 1). Our method combines theory, MD simulations and a novel interferometric technique [1], where all system parameters are finely tuneable and experimentally measurable, reaching extreme sensitivity in amplitude measurements (10^{-10} m). This approach enables dynamic interfacial characterisation (surface tension, charge, adsorption-desorption kinetics and surface distribution), for instance, of surfactant-covered bubbles [2].

Recent extension addresses the more intriguing case of two nearby oscillating bubbles (drops), whose solvent-mediated interactions are studied as a function of surface coverage and medium properties. These fluctuation-driven forces bear a resemblance to van der Waals interactions, but are less affected by electrostatic shielding and decay over much larger distances (10^{-4} m). Results suggest the potential application of our technique in biomimetic studies of cell-cell hydrodynamic interactions.

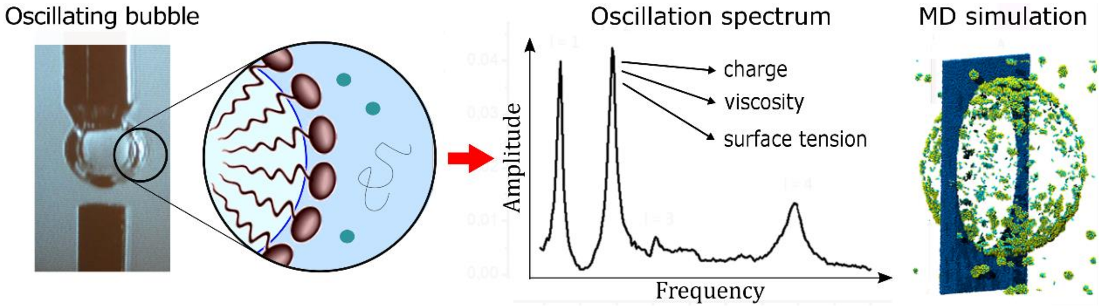

Figure 1. *Left,* a surfactant-coated, millimetre-sized air bubble oscillating in aqueous environment. *Centre,* the oscillation spectrum yields interfacial properties. *Right*, surface distribution obtained by MD simulation.

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OR-18

Solvent-free Pd-catalyzed heteroaryl-aryl coupling reactions via C−H bond activation

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Palladium-catalyzed direct arylation *via* aromatic C-H bond activation is one of the most attractive ways for synthesizing complex organic molecules [1]. In particular C-H arylation represents a versatile approach for step-economical synthesis of diverse biaryl motifs with respect to traditional cross-coupling reactions avoiding the use of preformed organometallic reagents, which are sensitivite to air and moisture, expensive and, often, toxic. In this context, we have reported a thiophene-aryl direct coupling reaction in a green, convenient, and inexpensive deep eutectic solvent, a choline chloride/urea mixture [2]. As an alternative approach, solvent-free palladium-catalyzed direct arylation reactions would provide an environmentally attractive procedure for the preparation of biaryls. In fact, solvent-free conditions not only avoid the hazards and toxicity associated with the use of solvents, but also reduce energy costs due to shorter reaction times, and simplify reaction procedures and workup.

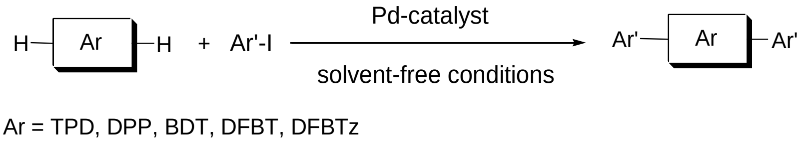

Figure 1. Pd-catalyzed direct coupling reactions via C−H bond activation in solvent-free conditions.

The reaction is performed in non-anhydrous conditions and without exclusion of air and tolerates a number of functional groups on both coupling partners. Thieno-pyrrole-4,6-dione (TPD), diketopyrrolopyrrole (DPP), benzodithiophene (BDT), 5,6-difluorobenzo[1,2,5]thiadiazole (DFBT) and 5,6-difluoro-2-heptadecyl-2H-benzo[d][1,2,3]triazole (DFBTZ)-based cores as the C−H activated substrate have been used (figure 1), in consideration of their interest in the construction of donor - acceptor molecular and polymeric semiconductors for optoelectronics applications [3].

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OR-19

Multivalent glycomimetics: anchoring iminosugars on dendrimeric and globular scaffolds

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Iminosugars are excellent chemical tools for investigating glycosidase inhibition, due to their ability to mimic the natural substrate during the glycosidase transition state involved in biological process [1]. This leads to several interesting biomedical applications, such as treatment of different pathologies (for example bacterial and viral infections) or of metabolic disorders such as diabetes and Lysosomal Storage Disorders (LSDs) [2]. Recently, the inhibitory activity of iminosugars towards some therapeutically relevant glycosidases has been successfully enhanced by assembling them in multivalent architectures containing several iminosugar warheads linked together to a common scaffold [3].

Here, two types of iminosugar inhibitors were multimerized onto different scaffolds, dendrimeric and micellar. Preliminary biological data towards commercially available and lysosomal glycosidases are also reported.

N-alkyl trihydroxypiperidines 1 bearing an azido terminal moiety (Fig. 1) were multimerized onto different propargylated scaffolds through CuAAC click reaction and preliminary inhibition tests against human α-glucosidases were performed. The same bioactive warhead was also employed in the design of micellar aggregates. Different examples of multivalent structures were prepared using pyrrolidine iminosugar DAB-1 derivatives 2 properly functionalized to be anchored to gold glyconanoparticle cores.

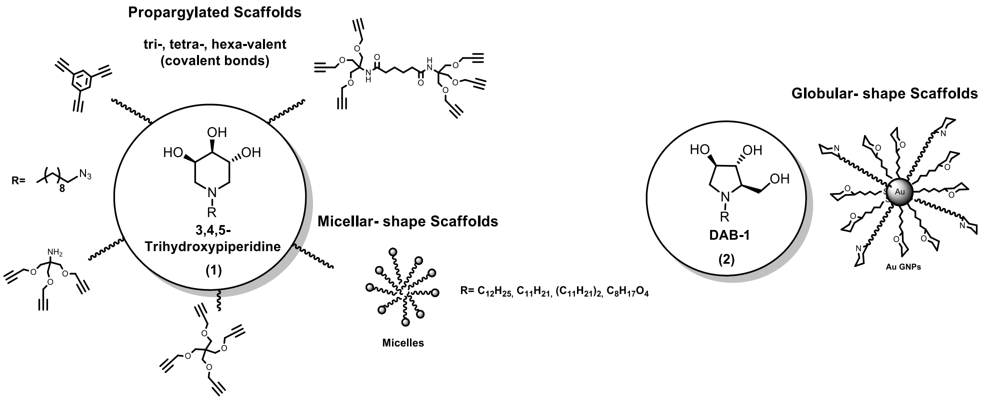

Figure 1. Two iminosugars multimerized onto different type of scaffolds.

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OR-20

Design, synthesis and characterization of fluorinated gold nanoparticles as theranostic agents

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One of the actual trends in the novel field of nanomedicine is centred on the development of "theranostic" nanosystems, capable of performing both the diagnosis and the treatment jobs for a specific pathology. We took up the challenge, working on the realization of a nanoplatform for magnetic resonance imaging (MRI) that features a gold core covered with ligands composed of a fluorinated oxyethylene portion. This polymer has been specifically designed to provide chemically equivalent fluorine nuclei for ^{19}F-MRI and binding for drug molecules, foreseeing the implementation of controlled delivery and release functions [1].

The first results achieved were improved with the synthesis of a linear ligand containing a perfluoropolyether (PFPE) portion with 44 ^{19}F nuclei. This ligand, along with a second one built to carry a BODIPY fluorescent unit, have been used in a modified Brust-Schiffrin procedure [2] for the synthesis of mixed monolayer gold nanoparticles with a core around 2-3 nm in diameter (Figure 1). These nanosystems have been studied by means of TEM, TGA, ^{19}F-NMR, UV-VIS for release kinetics and incubation with HeLa cells to assess their cytotoxicity. The outcomes have been promising in terms of structure stability, NMR response and biological interactions.

The future research work is aimed at introducing an even higher number of fluorine nuclei, through the modification of the basic structure of the ligand.

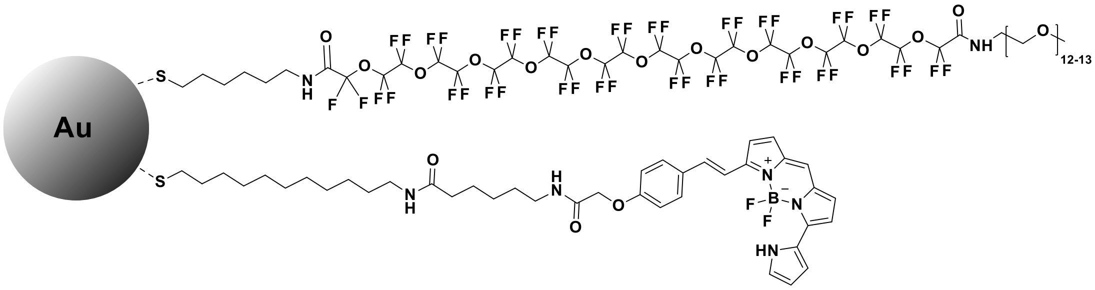

Figure 1. Representation of the structure of the ligands attached to the gold nanoparticle.

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OR-21

Triterpenoids hydroxamates as HIF prolyl hydrolase inhibitors

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The carboxylate-to-hydroxamate transformation had a remarkable effect on the biological profile of pentacyclic triterpenoid acids (PCTTA). Affinity for the transcription factors targeted by the natural compounds (NF-kB, STAT3, Nrf2, TGR5) was de-emphasized, while inhibitory activity on HIF prolyl hydrolases was selectively induced. Activity was reversible, isoform-selective, dependent on the hydroxamate location on the triterpenoid scaffold, and unremarkable when this element was replaced by other chelating groups. The hydroxamate of betulinic acid (**Figure 1**) was selected for further studies, evaluating its effect on HIF-1α expression under normal and hypoxic conditions, its pattern of induction of HIF-dependent gene-expression and angiogenesis, and its neuroprotective activity in vitro. The positive results obtained provided a rationale to evaluate the hydroxamate of betulinic acid in a murine model of neuronal striatal degeneration, qualifying it as a promising agent for further development.

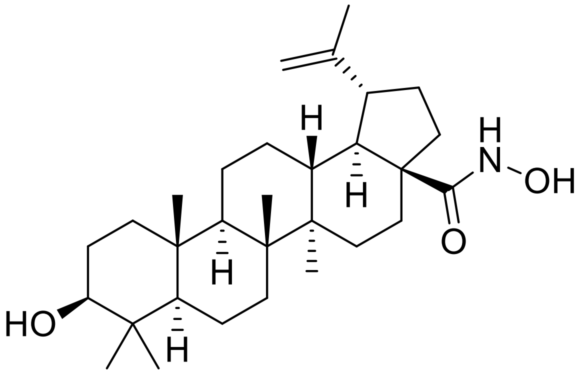

Figure 1. Hydroxamate of betulinic acid.

OR-22

Structural characterization of regenerated silk fibroin through $CeCl_3$ solubilization protocol

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Silk is a fibrous protein polymer spun into fibers by different animals, characterized by extraordinary mechanical properties, such as high tensile strength and extensibility, as well as biological compatibility. This mechanical superiority is thought to be dependent on the molecular assembly of silk fibrins. Among them, *Bombyx mori* silk fibroin (SF) represents the most easily available and interesting silk [1]. XRD pattern reveals a micrometric crystallite domain made of antiparallel β sheet polypeptides, further arranged in a nanometric symmetry along the fiber axis. SF is a difficult material to process. In fact, it requires a degumming step, then dissolution in 9.3M LiBr or 3.8M hydroalcoholic $CaCl_2$ solutions and finally a long dialysis procedure. Despite the enormous number of papers involving SF treatment, there is not yet a satisfactory rationalization of the dissolution process, neither a valid explanation of Li and Ca interactions with SF. Starting from the hypothesis that ion charges and ionic radii must play a key role in the whole process, we investigated lanthanide ions such as Ce^{3+} and Gd^{3+} due to the identical ionic radii of Ca^{2+} but exhibiting a bigger ion charge. In a completely unexpected way, we obtained a new fibrous material from dialysis of lanthanide treated SF, suggesting a Ce^{3+} intercalation between SF β-sheets. New fiber formation cannot be achieved with any reported treatment, since SF solutions gelify, completely losing a long-range hierarchical ordered structure.

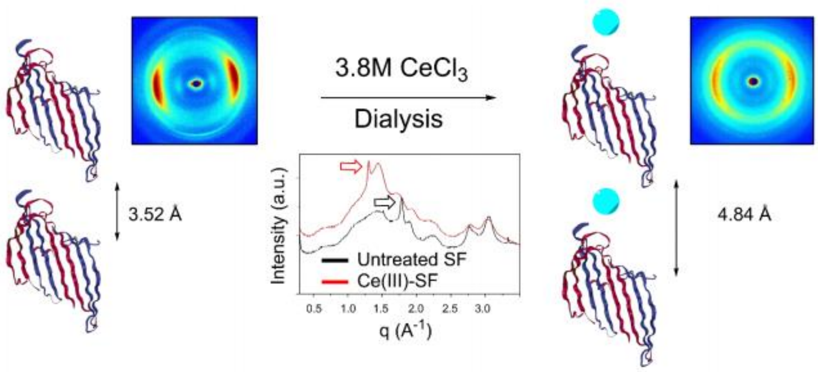

Figure 1. Schematic representation of Ce^{3+}(spheres) interaction with SF(β-sheets). XRD patterns are reported, with Graph showing peak shifting.

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OR-23

Tandem gold(I)-catalyzed cyclization for the synthesis of pentannulated N-hetero and carbacycles

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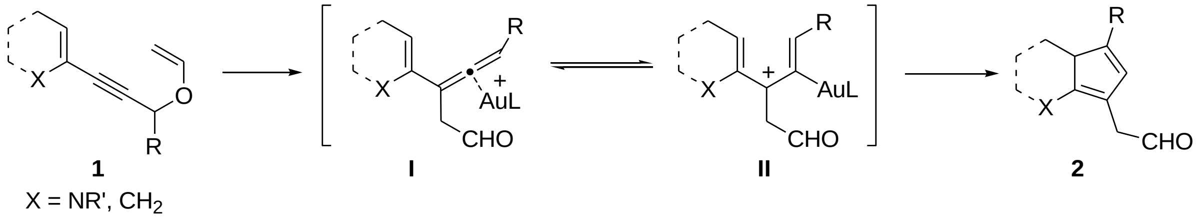
Transition-metal catalysis is widely used for making new bonds through a variety of processes and among these the most powerful are those which allow for the construction of complex frameworks through cascade processes in a single synthetic step. During the last two decades, the interest on homogeneous gold catalysis has rapidly grown through a kind of new "gold rush". The "alkynophilicity" of gold and its ability to prompt tandem processes has in fact led to complex cyclic frameworks useful in medicinal chemistry and agrochemical industry.

According to the previous works of our research group [1], we have developed a tandem gold(I)-catalyzed Claisen rearrangement/Nazarov reaction of enynyl vinyl ethers **1** which efficiently provides functionalized cyclopentadienes fused with various N-hetero and carbacycles (Scheme 1) [2]. Substrates of type **1** are designed to undergo a gold-catalyzed 3,3-rearrangement which generates allene intermediate **I**. This in turn undergoes a 4π-electrocyclization (Nazarov reaction) leading to the target compound **2**.

The reaction occurs under mild conditions and provides stable products with high regioselectivity and in good to excellent yields (up to 96%).



Scheme 1. Tandem gold(I)-catalyzed rearrangement/Nazarov reaction of enynyl vinyl ethers.

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OR-24

Natural deep eutectic solvents as an efficient catalytic system for the Nazarov cyclization

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The Nazarov cyclization (NC) consists in a conrotatory electrocyclization of divinyl ketones to cyclopentenones, catalyzed by Brønsted or Lewis acids, and represents one of the most useful synthetic tools for the preparation of cyclopentenone motifs [1-3]. However, the reaction has some drawbacks, most prominently the use of strong Brønsted acids which are usually toxic and the use of volatile organic compounds (VOCs) as solvents. To date, advances on more sustainable versions of the NC are limited to very few reports [4-5]. Natural deep eutectic solvents (NADES) have recently emerged as a new promising class of green solvents, not only because of their low cost, low toxicity and biodegradability, but also because they can have an active role in promoting organic reactions [6-7]. Here, we report our study on the Nazarov cyclization in various acidic deep eutectic solvents, employing non-toxic naturally occurring carboxylic acids as components of the catalytic system.

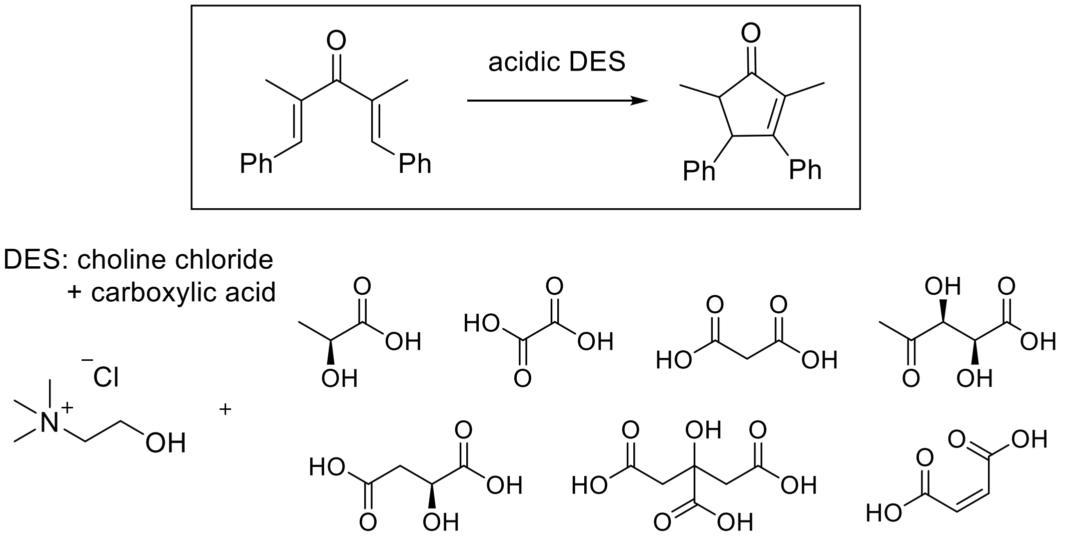

Figure 1. The Nazarov cyclization in acidic deep eutectic solvents.

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OR-25

Supramolecular detection of nerve agents simulant: from mono-topic to multi-topic approach

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Nerve agents are some of the most toxic chemicals used as weapons. The recent international scenario demonstrates that the sensing of Chemical Warfare Agents (CWAs) is still an important goal for human health and safety. Dimethoxymethylphosphonate (DMMP) has emerged as one of the best Nerve Agent stimulant. Today, detection of these simulants by a supramolecular approach is an important target due to the high rate and selectivity of the recognition process [2]. Here new receptors based on metal salen complexes, able to recognise DMMP by using a supramolecular approach are reported. We exploited a Lewis acid-base interaction between an uranyl ion in the salen scaffold and the phosphate group of the simulant. In order to improve binding affinity and selectivity, multi-topic receptors were designed and synthesized. In addition to the Lewis acid-base interaction, the formation of two additional hydrogen bonds leads to higher binding constants and excellent selectivity. Furthermore, the presence of Zn ion as metal centre allows to detect DMMP via emission spectroscopy [3].

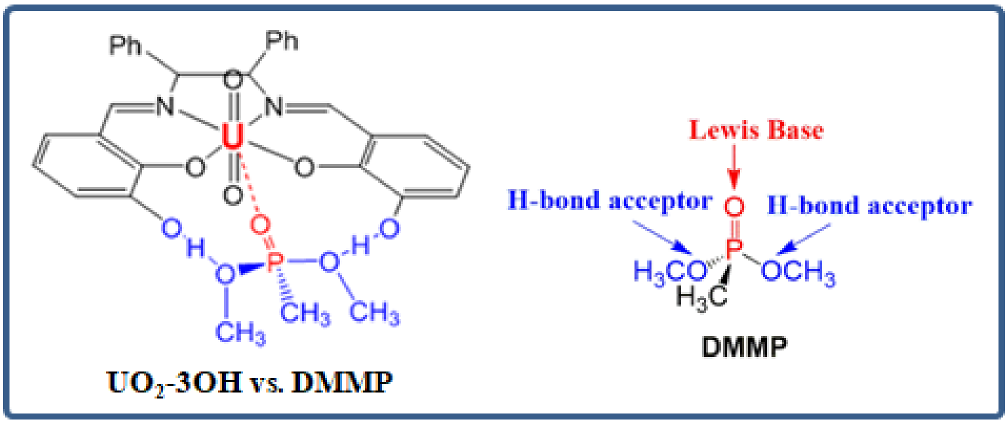

Figure 1. Supamolecular complex of di-topic receptor and DMMP.

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OR-26

A new class of solvents for sustainable cellulose functionalisation

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Ionic liquids (ILs) are salts composed of an organic cation and an organic or an inorganic anion which are liquid at or near room temperature. ILs have attracted a great deal of interest in the last 20 years due to some unique physicochemical properties such as the large electrochemical window, the chemical and thermal stability, the negligible volatility, and the no flammability, to mention a few. Polysaccharides such as cellulose, chitosan and chitin are highly abundant renewable feedstocks and represent a potential solution (and challenge at the same time) for the replacement of traditional fuel and plastic material. ILs are typically used for polysaccharides processing and functionalisation due to their unique physicochemical properties, and to their capability to dissolve them [1].

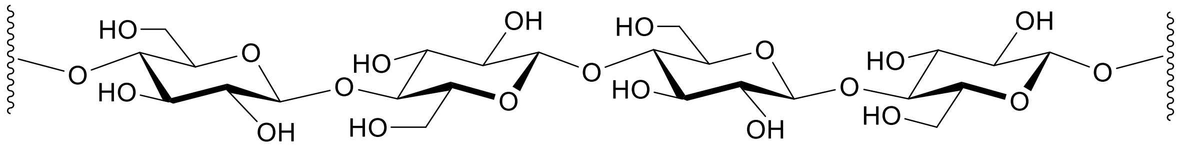

Figure 1. Structure of cellulose.

Indeed, ILs are one of the few solvents able to disrupt the native hydrogen bonds present within the biopolymers [1], thus allowing their dissolution and further modification [2].

Herein, we report the development of new bio-based ionic liquids through an easy, single step, environmentally friendly procedure, which has the potential to be scaled-up. Three different classes of ILs, showing a remarkable ability of dissolving cellulose, will be discussed. The chemical modification of cellulose promoted by ILs, which allowed for the obtainment of new bio-based materials, will be also presented.

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OR-27

Intrinsically photoswitchable α/β peptides toward two-state foldamers

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The field of foldamers has been characterised by the expansion of conformationally controlled molecules aimed at developing novel non-natural structural features, with the purpose of achieving new biomimetic function [1]. A classic model of foldamer is designed to adopt a single restricted conformation, while there are not reported examples of backbone-conformation interchanged foldamers. We have recently shown that incorporation of a simple fumaramide (human metabolite) or maleamide residue into a peptidomimetic foldamer renders the foldamer conformation intrinsically photosensitive and allows it to exhibit a functional response as a result of photochemical irradiation at an appropriate wavelength [2]. In particular, we found that the fumaramide or maleamide residue provides a conformationally insulating or conducting device, alternatively preventing or allowing the transmission of stereochemical information from a chiral fragment linked to one side of the unsaturated system to a helical peptide domain. Within our recent work we want to expand the ability on the photo-induced control of conformational switches in appropriately designed foldamers based on (*E*/*Z*)-3-aminoprop-2-enoic acid [or (*E*/*Z*)-3-aminoacrylic acid] directly incorporated in the foldamer backbone, thus allowing them to dynamically interchange when present in their *E* or *Z* isomeric conformations. As a proof of concept, *E*/*Z* photoisomerization of a 3-aminoprop-2-enoic acid residue, inserted as the junction between two conformationally distinct peptide domains (one helical while the other β-sheet promoter), allowed supramolecular self-association to be reversibly turned on/off [3].

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OR-28

Synthesis of polycyclic quinolines by means of Brønsted acid catalyzed reaction of β-(2-aminophenyl)-α,β-ynones with ketones

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The quinoline ring represents an important structural motif in many bioactive and natural compounds. Various quinoline derivatives have found application in medicinal chemistry, and quinoline-based molecules are also useful intermediates in assembling new materials with interesting electronic properties [1]. As a consequence, several synthetic procedures have been developed. However, the reported procedures face some serious drawbacks, such as harsh conditions, low yields and the commercially limited availability of reagents. Because of this, more efficient methods for the synthesis of substituted quinolines are needed. Herein we would like to report the results of our further investigations on the use of β-(2-aminophenyl)-α,β-ynones as versatile building blocks [2,3] in the development of a novel valuable approach to the synthesis of polycyclic quinolones through their acid-catalyzed reaction with carbonyl compounds under operatively simple reaction conditions (Figure 1).

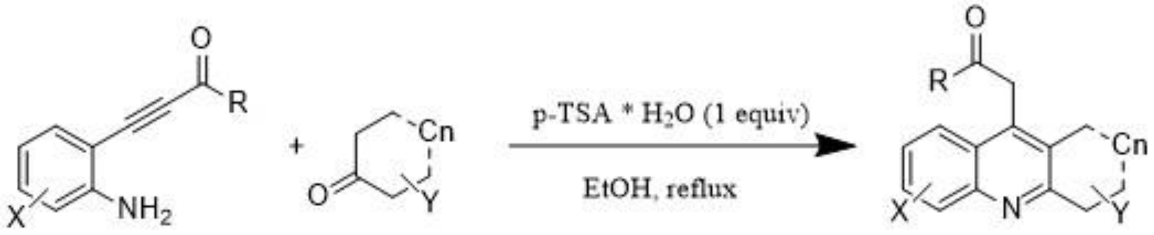

Figure 1

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OR-29

Substituent effect on the direct photodegradation of benzotrifluorides

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Benzotrifluoride moieties are used since last decade in many pharmaceutical and agricultural products [1]. In the last 10 years, the turnover generated by benzotriluoride drugs increased tenfold [2], naming them as a new class of potential water contaminants. In these terms, it is crucial to understand their environmental fate. Recent literature showed that benzotrifluorides are not stable under UV irradiation and convert into benzoic acids [3]. It was also suggested that the ring substituent may play an important role on the reactivity of the CF_3 moiety [3], but a direct correlation between substituents and photo-reactivity was never established. In this study we explore the structure-activity relationship between ring substituent and direct photolysis rates to provide a tool to conscientiously design new drugs and pesticides and understand the fate of those already commercialized and used.

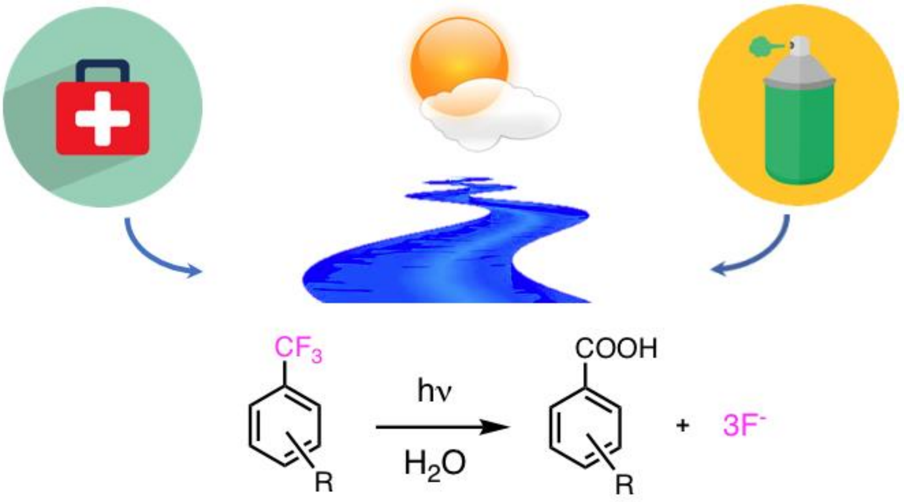

Figure 1. Direct photodegradation of benzotrifluoride derivatives in water.

[1] F.M.D. Ismail, *J. Fluorine Chem.* **118** (2002) 27-33.
[2] N.A. McGrath, M. Brichacek, J.T. Njardarson, *J. Chem. Ed.* **87** (2010) 1348-1349.
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OR-30

Application of carbon nanotubes to tissue regeneration

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As concerns the application of carbon nanotubes in tissue regeneration, our work has been focus on spinal cord injury, this damage often causes permanent changes in strength, sensation and other body functions below the site of the injury. From a therapeutic viewpoint the glial scar (a lesion formed after the injury) creates a barrier for the regeneration of injured axons in which proteoglycans play a key inhibitory role in the regeneration process. The key in our proposal is that it should be possible to develop an innovative chemical strategy for the removal of the inhibitory molecules chondroitin sulfates, providing beneficial effects on axons regeneration. We have designed nano-devices, consisting of "polycationic structures" assembled around a central backbone made of carbon nanotube, thus creating what we name nano-sponges [1]. Finally, we have proposed the decoration of our nano-sponges with magnetic iron oxide nanoparticles [2]. The IO–NCM composites will stick stably to chondroitin sulfates, thereby making the glycosaminoglycans magnetic. The latter will be separated from the glial scar without destruction under the action of an external magnetic field.

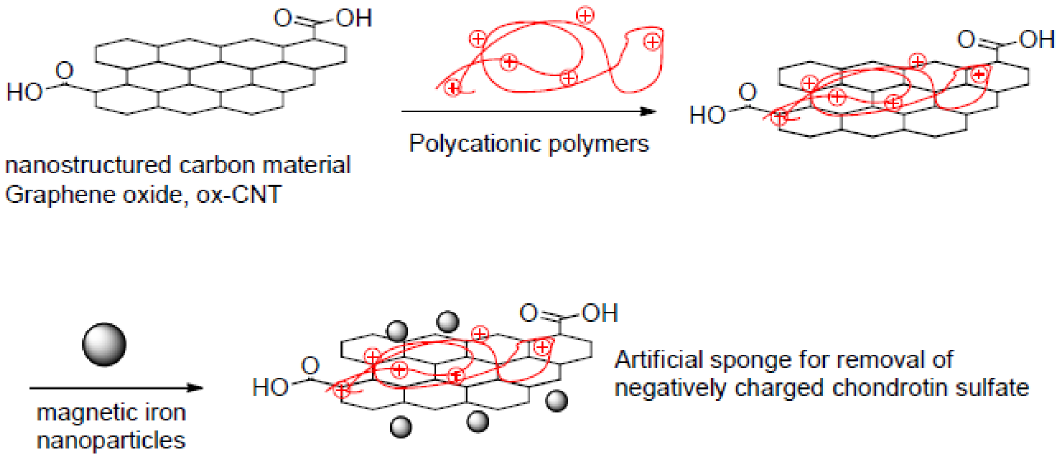

Figure 1. General structure of magnetic artificial sponges based on nanostructured carbon material.

[1] L.W. Place, M. Sekyi, M.J. Kipper, *Biomacromolecules* **15** (2014) 680-689.
[2] W. Zhang, X.D. Zuo, W.D. Wu, *Rev. Adv. Mater. Sci.* **40** (2015) 165-176.

OR-31

Microwave-assisted synthesis of 1,4-pentanediol over Au catalysts: a metal/support coordinative effect

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The demand for renewable sources has steadily increased over the last two decades, though chemical industry still runs mainly with fossil feedstock. Biomass has been recognized as a worldwide renewable source of fixed carbon for the production of platform chemicals. In this context, the exploitation of residual lignocellulosic material could drive to zero-waste production processes via cascade protocols, one of the hottest goals of current research. Levulinic acid (LA), a sugar derived keto-acid (4-oxopentanoic acid), is a key intermediate for the production of fine chemicals and biofuels. A large number of value-added chemicals can be synthetized from LA, namely fuels, solvents, fragrances, polymers, resins, pharmaceuticals. Several LA transformations pass through γ-valerolactone (GVL), directly used (fragrance, fuel and food additive) or applied as an intermediate in fine chemicals synthesis (i.e. 1,4-pentanediol, PDO) [1]. Only few reports described the hydrogenation of GVL to 1,4-PDO, as the reaction outcome is affected by the intrinsic stability of lactone ring. New catalytic systems able to act simultaneously on hydrogen dissociation and ring activation are requested. 1,4-PDO, as other diols, has an important commercial value for biodegradable polyesters and intermediates.

Herein we report LA hydrogenation over two gold catalysts (commercial 1 wt% Au/TiO_2 by AUROlite™ and 2.5 wt% Au/ZrO_2) in neat conditions or in aqueous media under microwave (MW) irradiation in the presence of either H-donors (methanol, propanol or formic acid) or molecular H_2. Au/ZrO_2 catalyst showed promising activity in H-transfer reactions, leading selectively to GVL with formic acid (produced 1:1 mol with LA from glucose). The reaction under H_2 pressure, with Au/TiO_2, converted completely LA to GVL and partially to PDO already at 150 °C. Complete selectivity is reached at higher temperature. The nature of the support may strongly affect the selectivity to GVL rather than PDO. Gold nanoparticles (NP) have been characterized by HRTEM, XRD, FTIR and UV-Vis measurements. A reaction mechanism focused on the cooperative role played by the Au NP and the support will be discussed.

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[1] S. Tabasso, G. Grillo, D. Carnaroglio, E. Calcio Gaudino, G. Cravotto, *Molecules* **21** (2016) 413-422.

OR-32

Structure beyond sequence: which role for miRNA conformations?

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MicroRNAs (miRNAs) are a class of highly conserved, short and non-coding single-stranded RNA, with a crucial role in different cellular and metabolic pathways. To date, over 2000 miRNAs have been identified in humans, targeting more than 30% of the human genome. Their aberrant expression levels were often associate to the initiation and development of human diseases, genetic disorders, and altered immune system functions [1]. Therefore, miRNAs are emerging as novel biological targets for chemists, biochemists and bioinformatics to design synthetic microRNAs able to target multiple genes and consequently to find therapies for diseases caused by miRNAs dysregulation [2]. Although in the last years many studies have been devoted to understand the miRNA activity, their mechanism of action have not been fully understood. In this contest great interest is taken on the structures adopted by miRNAs. Indeed, nucleotide sequence of miRNA could not be the sole determining parameter for miRNA-binding specificity. The potential arrangement of miRNAs on 3D structures can act as an additional tuning level of post-transcriptional regulation, influencing the affinity and the specificity for their target [3]. By Circular Dichroism, spectroscopic experiments it is possible exploring the presence in solution of structures different from single-stranded arrangements. Our preliminary data on some endogenous and synthetic miRNAs, seem to suggest the presence of several complex structures, which could be crucial for the action mechanism beyond the simple sequence of nucleotides.

Figure 1. Cartoon of miRNA sequence *vs* structure.

[1] H. Dong, J. Lei, L. Ding, Y. Wen, H. Ju, X. Zhang, *Chem. Rev.* **113** (2013) 6207-6233.
[2] A. Laganà, M. Acunzo, G. Romano, A. Pulvirenti, D. Veneziano, L. Cascione, R. Giugno, P. Gasparini, D. Shasha, A. Ferro, C.M. Croce, *Nucleic Acids Res.* **42** (2014) 5416-5425.
[3] A. Belter, D. Gudanis, K. Rolle, M. Piwecka, Z. Gdaniec, M.Z. Naskręt-Barciszewska, J.Barciszewski, *PLoS One* **9** (2014) art. no e113848.

OR-33

Investigation on Zn(II) and Cu(II) binding sites in C4YJH2, a putative metal transporter of *Candida albicans*

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The necessity of new antifungal agents is unarguable, since current therapeutic treatments are not always effective due to the development of drug resistance. Nevertheless, the assimilation of metal nutrients from the host environment is a fundamental aspect of infections and deeper insights into the mechanism of metal uptake and transport in fungal species can provide crucial information to design new antifungal drugs [1].

From this perspective, we recently studied Zn(II) and Cu(II) binding behavior towards C4YJH2, a protein sequence of 199 amino acid residues, found in the genome of *Candida albicans*. Our previous work has confirmed that the main histidine-rich sequences between 131-148 (FHEHGHSHSHG SGGGGGG) and 157-165 (SHSHSHSHS) residues are involved in metal coordination [2].

In the native protein, the two His-rich domains are linked by the 9-residue sequence GSDHSGDSK, also containing a histidine and thus possibly contributing to the metal binding. Therefore, we decided to extend our investigation focusing on this "linker". The protected peptide Ac-GSDHSGDSK-NH_2 (148-156 residues) has been considered, along with its analogues Ac-GSDHSGASK-NH_2, Ac-GADHAGDAK-NH_2, Ac-GSDH-NH_2, Ac-HSGD-NH_2.

The preliminary results presented here concern the stoichiometry and thermodynamics of complex-formation of the above reported ligands with Zn(II) and Cu(II), investigated by means of potentiometric titrations; the hypothesized geometry of the formed species is also discussed, on the basis of UV-Vis and circular dichroism data at variable pH. The comparison among the behaviors of the different analogues helps to shed light on the role of specific residues in metal coordination geometry and complex stability.

[1] M. Blatzer, J.P. Latgé, *Curr. Opin. Microbiol.* **40** (2017) 152-159.
[2] D. Bellotti, D. Łoboda, M. Rowińska-Żyrek, M. Remelli, *New J. Chem.* **42** (2018) 8123-8130.

OR-34

Adsorption of L-lysine on L and ZSM-5 zeolites

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Zeolites are aluminosilicate minerals characterized by a regular crystalline structure with microporous cavities that confer a high superficial area. The physico-chemical properties of zeolites depend strongly on the composition of their framework, in particular, the hydrophilic/hydrophobic behaviour is affected by the SiO_2/Al_2O_3 ratio (SAR). Moreover, the different shape and dimensions of the internal channels and cages influence the adsorption selectivity towards host molecules [1].

The ability of zeolites to adsorb amino acids is of particular relevance in industrial biotechnology [2] due to the fact that these adsorbent materials could be used as solid solvents to stabilize the different charged forms of the amino acids. Moreover, these materials can also be employed in enrichment and separation of amino acids from complex mixtures.

In this work we evaluated the adsorption behaviour of zeolite L and ZSM-5 towards the amino acid L-lysine.

The two zeolites chosen present different framework structure; additionally, for the ZSM-5 two materials having different SAR were selected to study the effect of zeolite chemical composition on the adsorption capacity.

The results showed higher adsorption capacity for zeolites L with respect to ZSM-5, findings confirmed by TG/DTG/DTA analyses and XRD refinements.

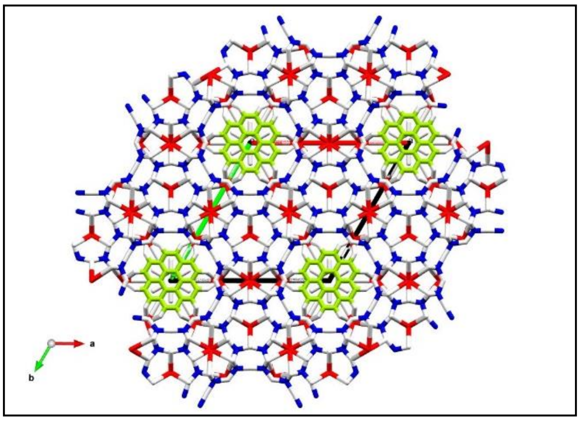

Figure 1. Structure of the *lysine-zeolite L* adduct.

[1] L. Pasti, E. Sarti, A. Cavazzini, N. Marchetti, F. Dondi, A. Martucci, *J. Sep. Sci.* **36** (2013) 1604-1611.
[2] K. Stückenschneider, J. Merz, G. Schembecker, *J. Phys. Chem*. C **118** (2014) 5810-5819.

OR-35

Methods for elemental analysis of PM samples collected on aluminum foils: results of an inter-comparison exercise

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Aluminum is the most common substrate in studies using PM impactors for the measurement of the number or weight of ambient air particles, as its characteristics ensure high collection efficiencies and cut-points equal to the ones declared by manufacturers. Nevertheless, the use of aluminum foils is not recommended when one of the purposes of the study is the analysis of the metal content of the sample [1,2]. The objective of this work was to develop an efficient elemental analytical procedure for the removal and acid digestion of particulate samples collected on aluminum foils by means of a cascade impactor, in order to perform the analysis of metals.

Two procedures were optimized, by using different digestion and analysis techniques; both procedures were then applied to the two halves of several Dekati Low-Pressure Impactor (DLPI) samples, and results were critically compared. Both the procedures include the removal of samples from the supports by using small cotton wads wet with nitric acid. The efficiency of the removal process was proved by further cleaning of aluminum foils after the removal of samples, while the efficiency of the digestion procedures was tested by means of two different CRMs. Passing-Bablok regression was used for method comparison, and the two procedures resulted to be not significantly different at a confidence level of 95% [3]. The choice of the cotton type and the leaching of cotton wads resulted crucial for the accurate determination of alkali and alkaline earth metal content in PM samples.

[1] Dekati Ltd., Substrates and filters for Dekati® impactors (vers 6.3), in Dekati® Accessory. 2016.
[2] A. Noel, G. L'Espérance, Y. Cloutier, P. Plamondon, J. Boucher, S. Philippe, C. Dion, G. Truchon, J. Zayed, *J. Occup. Environ. Hyg.* **10** (2013) 155-172.
[3] H. Passing, W. Bablok, *J. Clin. Chem. Clin. Biochem.* **21** (1983) 709-720.

OR-36

Thermodynamic comparison of zwitterionic teicoplanin-based 2µm superficially and sub-2µm fully porous particles for ultrafast chiral liquid chromatography

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The study and understanding of adsorption and enantiorecognition mechanisms between chiral analytes and stationary phases is essential for different reasons: pushing forward the limits of high efficient and ultrafast chiral liquid chromatography and understanding the basis of thermodynamics of adsorption [1]. In this work, thermodynamic performances of two zwitterionic teicoplanin-based chiral stationary phases (CSPs) prepared respectively on 2.0 µm superficially porous particles (SPPs) and on 1.9 µm fully porous particles (FPPs) of narrow particle size distribution (nPSD) have been analyzed and compared [2]. More in details, the adsorption isotherms of Z-D,L-Methionine enantiomers have been studied under Hydrophilic Interaction Liquid Chromatography (HILIC) mode by using the so-called Equilibrium Dispersive (ED) model [3]. The Inverse Method (IM) has been used for isotherm determination.

Results have shown the competitive Bi-langmuir isotherm model to be suitable for the description of the separation of Z-D,L-Methionine enantiomers on the two columns, indicating the presence of two different types of adsorption sites: one selective, responsible for the chiral recognition mechanism, and one nonselective, in which the two enantiomers behave the same. On the one hand, FPPs show higher selectivity values in comparison to SPPs, highlighting the greater enantioselective potential of these particles. On the other hand, SPPs are characterized by slightly larger selective and nonselective binding than FPPs. These data correlate with the specific loading of chiral selector, which was found to be larger on SPPs than on FPPs. This could negatively impact when moving to ultrafast separations.

[1] M. Catani, S. Felletti, O.H. Ismail, F. Gasparrini, L. Pasti, N. Marchetti, C. De Luca, V. Costa, A. Cavazzini, *Anal. Bioanal. Chem*. **410** (2018) 2457-2465.
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OR-37

Formation of metal-ligand complexes in atmospheric aerosol from an urban environment in Padua (Italy)

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Aqueous phase processing of aerosol can lead to substantial modifications of aerosol chemical and physical properties. A process potentially very important in this context is the formation of metal-organic ligand complexes in atmospheric aqueous phases, like fog/cloud droplets and deliquescent aerosol [1,2]. Organic ligands are already present in the aerosol, and by coordinating metal ions they can increase the solubility of metals [1] and therefore their bioavailability.

We investigated the formation of metal-organic ligand complexes in atmospheric aerosol from an urban background site in the city center of Padua (Italy), in the Po Valley. Aerosol samples were collected and characterized for quantification of both metals and organic ligands using state-of-the-art instrumentation. Speciation of metal-ligand equilibria in solution mimicking fog/cloud waters was done through a combined thermodynamic modelling and multivariate statistical analysis approach.

Preliminary results show that iron, copper and manganese are present in the aerosol in a complexed form, mainly with oxalate, malonate and succinate. Iron was the metal whose solubility was the most influenced by the presence of organic ligands. Dissolution kinetics of many metals were influenced by the environmental conditions during the campaign.

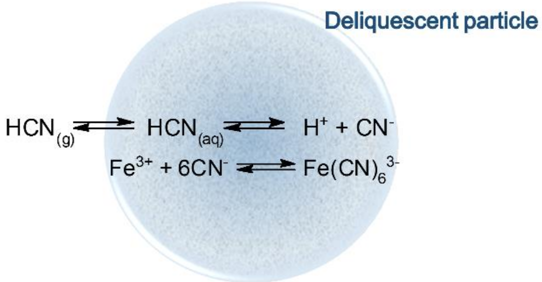

Figure 1. Example of metal-ligand formation processes [3].

[1] H. Okochi, P. Brimblecombe, *Sci. World J.* **2** (2002) 767-786.
[2] S. Scheinhardt, K. Müller, G. Spindler, H. Herrmann, *Atmos. Environ.* **74** (2013) 102-109.
[3] C. Giorio, D. Marton, G. Formenton, A. Tapparo, *Environ. Sci. Technol.* **51** (2017) 14107-14113.

OR-38

New electrochemical strategy for the preparation of layered double hydroxides (LDHs)

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Layered double hydroxides (LDHs) containing redox active transition metals are attractive compounds for electrochemical applications such as energy storage, sensors, fuel cells and catalysts for oxygen evolution reaction (OER) [1,2].

We here propose a novel and enhanced electrochemical route to deposit the LDHs through a potentiodynamic method. In all cases studied, it results highly reproducible and the LDHs display a greater crystallinity in respect to those electrodeposited with the more commonly used potentiostatic method [3]. The films obtained have been characterized by a large number of techniques (such as CVs, PXRD, Raman spectroscopy, SEM and XAS) in order to confirm the obtained phase.

The as synthesized electrodes have been tested as catalysts for oxygen evolution reaction displaying great performances.

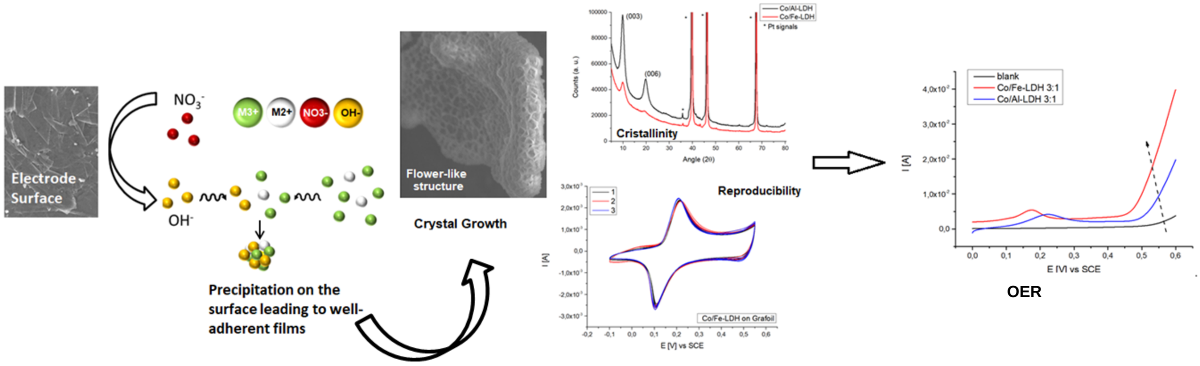

Figure 1. A schematic representation of the proposed work.

[1] Y. Vlamidis, E. Scavetta, M. Giorgetti, N. Sangiorgi, D. Tonelli, *Appl. Clay Sci.* **143** (2017) 151-158.
[2] Y. Vlamidis, E. Scavetta, M. Gazzano, D. Tonelli, *Electrochim. Acta* **188** (2016) 653-660.
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OR-39

Prebiotic synthesis of redox-active iron-sulfur catalysts

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Iron-sulfur clusters are indispensable to extant metabolism and are thought to have had an ancient role in mediating the chemical reactions that led to life. However, there has been no clear proposal for how these inorganic clusters came to occupy such an important position in biology.

We have previously described two critical steps in the iron-sulfur cluster assembly mechanism to be mediated by UV light coming from the young Sun. Moreover, the compatibility of the described chemical pathway for the synthesis of iron-sulfur clusters within model fatty acid protocells further suggests that biological iron-sulfur cluster assembly could have occurred at a very early phase in the evolution of life [1].

In modern biology, iron-sulfur clusters are mainly known as redox-active cofactors, able to catalyse one-electron transfer reactions exploiting the redox couple Fe(II)/Fe(III). Prebiotic iron-sulfur peptides could be then studied to reproduce extant metabolic reactions catalysed by iron-sulfur proteins in a prebiotically plausible way in order to determine the chemical roots of protometabolism. I will show that ferric ions coordinated by small organic thiols or cysteine-containing tripeptides can induce the oxidation of biologically relevant electron donors such as NADH and NADPH within fatty acid and phospholipid vesicles. The studied redox system was encapsulated within model protocells and implemented with electron acceptors such as ubiquinone, hydrogen peroxide and molecular oxygen, to determine the ability of iron-sulfur species to undergo consecutive redox cycles. Moreover, a proton gradient induced by hydrogen peroxide and molecular oxygen reduction was detected, suggesting that iron-sulfur systems could serve as plausible prebiotic models of the prebiological steps leading to modern biological ion pumps [2].

[1] C. Bonfio, L. Valer, S. Scintilla, S. Shah, D.J. Evans, L. Jin, J.W. Szostak, D.D. Sasselov, J.D. Sutherland, S.S. Mansy, *Nat. Chem.* **9** (2017) 1229-1234.
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OR-40

From liquid crystals to microrobotic legs and hands

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Mimicking human abilities is a great challenge in robotics and soft materials are gaining interest to bridge the gap between humans and machines. If the goal is to realize a device in the microscale, even stronger efforts are needed to overcome both, technological (e.g. fabrication and assembling) and physical issues (e.g. adhesion plays a major role).

Thanks to the use of light, we were able to approach these problems and to present new remotely controlled microrobots. Starting from simple liquid crystalline monomers, a light-deformable material can be patterned in a 3D fashion by the use of Direct Laser Writing. The elastic reshaping properties of such polymer are able to mimic muscle-like functions allowing for the fabrication of micro-walker, performing surface-dependent walking on different surfaces [1], or micro-hands, able to catch microparticles [2].

Very interestingly, the micro hand can distinguish between particles of different colors and decide autonomously to grab or not an object in its vicinity. This concept constitutes a crucial element for the development of intelligent devices performing tasks without human intervention.

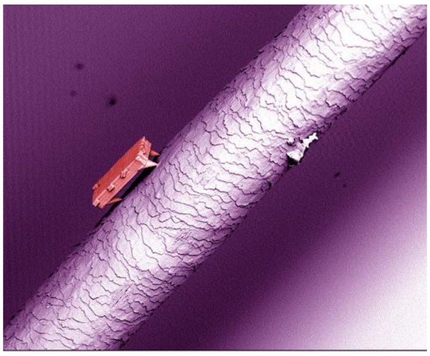

Figure 1. A microscopic walker up to a human hair.

[1] H. Zeng, P. Wasylczyk, C. Parmeggiani, D. Martella, M. Burresi, D.S. Wiersma, *Adv. Mater.* **27** (2015), 3883-3887.
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OR-41

Dissection of the folding pathway of a G-rich region within c-KIT promoter

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G-quadruplexes (G4) within oncogene promoters are promising anticancer targets since it has been observed that they can modulate oncogenes transcription. However, often they undergo complex structural rearrangements that prevent a precise description of the optimal target. Moreover, even when high resolution structures are available, they refer to the thermodynamically stable forms but little or no information is supplied about their complex multistep folding pathway [1].

To dissect this issue, we chose kit2, a G4 forming sequence within c-KIT oncogene, as a case study following its kinetic behavior in the presence of K^+ and Na^+ ions. By means of a set of complementary spectroscopic and biophysical studies, we characterized the whole folding pathway of kit2 G-quadruplex. We identified a short-lived intermediate responsible for the G4 folding process in the presence of K^+ and Na^+ ions. After this initial folding step, kit2 undergoes to different folding pathways depending on the salt conditions. In Na^+-containing solution it follows a linear folding pathway achieving an antiparallel G4 arrangement. Remarkably, in K^+-containing solution a branched pathway is required to drive the wild type sequence to distribute between a monomeric and dimeric parallel G-quadruplexes [2].

Our approach has allowed us to identify transient forms whose relative abundance is regulated by the environment; some of them are characterized by a half-life within the timescale of physiological DNA processing events and thus may represent possible unexpected targets for ligands recognition.

Acknowledgment: This work was supported by University of Padova.

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OR-42

Metal-free α-trifluoromethylthiolation and α-trifluoromethylselenolation of carbonyl derivatives

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The incorporation of a SCF_3 or a $SeCF_3$ group into organic molecules is a topic of great interest, especially for the pharmaceutical and agrochemical industries [1,2]. Due to their high lipophilicity and high electron-withdrawing character (Hansch lipophilicity parameter $\pi_R = 1.44$ (SCF_3) vs $\pi_R = 1.29$ ($SeCF_3$)), these moieties represent a powerful opportunity to influence the pharmacokinetics properties of a drug molecule.

In the last years, new structural units, rising from the association between chalcogens and fluorinated moieties, have been introduced into carbonyl compounds, as emerging class with potential applications on several fields. New reagents have been developed as sources of electrophilic SCF_3 and $SeCF_3$ groups; however, a widespread use of such fluorinated compounds is hampered by the very limited number of strategies available for their preparation. In this contest, we have developed two methodologies for the preparation of α-SCF_3 [3] and α-$SeCF_3$ substituted carbonyl derivatives starting from non activated ketones or their derivatives (Fig. 1).

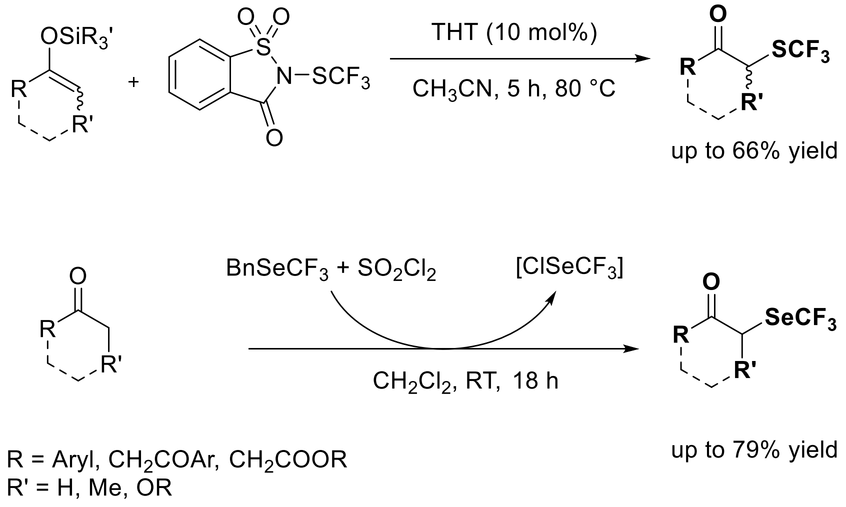

Figure 1. α-trifluoromethylthiolation and α-trifluoromethylselenolation of carbonyl derivatives.

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OR-43

Silver nanocubes for reproducible and controlled raman detection of proteins

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Standard Surface Enhanced Raman Spectroscopy (SERS) resides in the enhancement of the target by hot-spots randomly located on the nanosurfaces. In this work, we used silver nanocubes to generate regular hot spots located on the nanocubes corners. Proteins selectively interact with this hot-spots while maintain their native folding. In this hot-spots, proteins experience an intense E-field, which greatly improve the SERS efficiency and detection sensitivity [1]. Moreover, the interaction of proteins with nanocubes flat surfaces, where the E-field is less intense, is forbidden by the presence of a thick layer of polyvinylpirrolidone (PVP) polymer, as outlined by computational simulations and by electron microscopy analysis [1,2].

This strategy allowed a site-selective detection of proteins in their native state with a strong Raman signal enhancement, giving the possibility to reproducible and controlled SERS detection of proteins.

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OR-44

Scaling-up electronic spin qubits into extended molecular frameworks

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Practical implementation of highly coherent molecular spin qubits for challenging technological applications, such as quantum information processing or quantum sensing, requires precise organization of electronic qubit molecular components into extended frameworks. Realization of spatial control over qubit−qubit distances can be achieved by coordination chemistry approaches through an appropriate choice of the molecular building blocks. However, translating single qubit building units into extended arrays does not guarantee *a priori* retention of long quantum coherence and long spin−lattice relaxation times due to the introduced modifications over qubit−qubit reciprocal distances and molecular crystal lattice phonon structure.

Here we report on the preparation of a three-dimensional (3D) metal−organic framework (MOF) based on vanadyl qubits, [VO(TCPP-Zn_2-bpy)] (TCPP = tetracarboxylphenylporphyrinate; bpy = 4,4′-bipyridyl) (**1**), and the investigation of how such structural modifications influence qubits' performances. This has been done through a multitechnique approach where the structure and properties of a representative molecular building block of formula [VO(TPP)] (TPP = tetraphenylporphyrinate) (**2**) have been compared with those of the 3D MOF **1**. Pulsed EPR measurements on magnetically diluted samples in titanyl isostructural analogues revealed that coherence times are retained almost unchanged for **1** with respect to **2** up to room temperature, while the temperature dependence of the spin−lattice relaxation time revealed insights into the role of low-energy vibrations, detected through terahertz spectroscopy, on the spin dynamics [1].

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OR-45

Optimization of grafting SBA-15 synthesis for Levulinic acid production

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Transformation from a fossil fuel based economy to one based on renewable resources is one of the greatest 21st century challenge that industry has to face. Biomass utilisation has gained considerable interest in this sense, for its high potentiality as a resourceful substrate both for chemicals and fuels. Nonetheless, catalysis covers great importance in the development of efficient yet sustainable processes for biomass exploitation.

In this work, the attention has been focused on the valorisation of lignocellulosic biomass for the productions of levulinic acid [1]. Cellulose based materials have been employed as substrate and its transformation, characterised by hydrolysis reactions, can be catalysed by either homogeneous or heterogeneous acid catalysts. However, the potentiality of a heterogeneous catalyst is huge, since it avoids rig corrosion and problems of regeneration. The aim of this work is the development and optimisation of synthetic procedure to produce heterogeneous solid acid catalysts based on SBA-15. To achieve acid properties on SBA-15 material, grafting method, using 3-Mercaptopropyltrimethoxysilane (MPTMS), was carried out focusing the attention on the role of different solvents. Esane, Toluene and a mixture of water and NaCl were evaluated in this study [2,3]. Materials were characterised using different experimental techniques such as N_2-physisorption, FTIR and TEM. Catalytic tests were conducted in a stainless still autoclave in the 160 °C- 200 °C temperature range.

It was found that solvent highly affects morphological and chemical features of the materials; in particular, the best catalytic results were obtained with the catalyst prepared in water and NaCl, as this solvent allows to guarantee the best distribution of sulfonic groups over the surface leading to the best acid catalyst.

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OR-46

From the tumor microenvironment to the development of an innovative technology

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In the last decades glycoscience has strongly influenced biotechnology and medicine. For instance, the applications of glycoconjugation span glycan arrays for diagnostic purposes, metabolic labelling of glyco-architectures, adjuvants and carbohydrate-based drugs and vaccines [1]. On the contrary, in oncology the up-regulation (compared to normal cells) of specific glucose transporter proteins is still an untapped phenomenon from the therapeutic point of view. This is known as “Warburg effect”, a key strategy by which malignant cells can gain a larger glucose uptake in order to fuel accelerated glycolysis, and makes such transporters pharmacological targets suitable for the design of cancer-selective drugs [2].

Considering this feature of the tumor microenvironment and that the more aggressive the cancer, the higher the glucose requirement, we designed and started to develop new "smart" therapeutic agents and nanoformulations for the treatment of various malignancies.

The patented antitumor weapons can act as a kind of Trojan horse by means of two strategies wherein the carbohydrate moiety anchors the bioactive cargo to cancer cells [3].

The results collected so far in terms of preliminary in vivo toxicological profile and in vitro anticancer activity are very promising (IC50 values in the low micromolar or sub-micromolar range towards a panel of so-called “orphan” tumor indications), thus laying the foundation for a tech transfer process.

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OR-47

Luminescence modification via co-crystals formation: a crystal engineering approach

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A turning point in the search for purely organic luminescent materials has come from crystal engineering [1]. Co-crystallization of PAHs with halogenated co-formers has proved to be successful in lighting up phosphorescence in the solid-state [2, 3],which compared to fluorescence is a more rarely observed phenomenon in organic materials.

Here we report on newly synthesized co-crystals, obtained by reaction of an organic emitting molecule with the halogenated co-formers halo- or 1,4-dihalopentafluorobenzene. All materials have been synthesized by solvent-free methods, including mechanochemistry and crystallization from the melt, and characterized by XRD techniques, Raman, and luminescence spectroscopy in the solid state, see Figure 1. Rietveld analysis and RAMAN spectroscopy have proved particularly useful to evaluate sample purity, which is crucial for a reliable photophysical characterization, therefore allowing to identify and select the best synthetic strategy for each compound.

In contrast to the parent compound, which exhibits both fluorescence and phosphorescence emission in the solid-state, our co-crystals exhibit exclusive and strong phosphorescence emission, with a remakable lifetime.

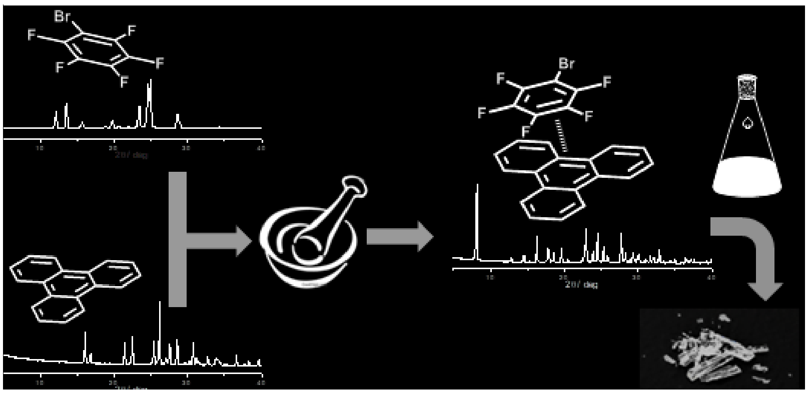

Figure 1. Mechanochemistry and seeding.

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OR-48

Unraveling surface basicity and bulk morphology relationship on covalent triazine frameworks with unique gas adsorption and catalytic properties

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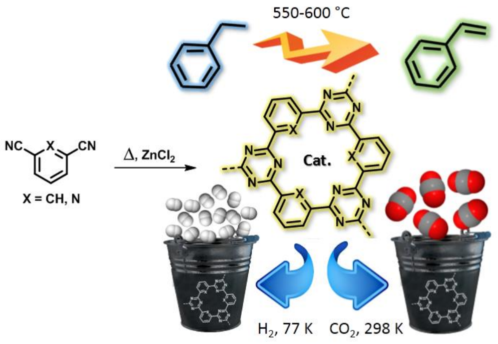
Porous organic polymers (POPs) have recently gained great attention thanks to their peculiar features such as their large surface area and their superior thermal and chemical stability. Among them, Covalent Triazine Frameworks (CTFs) represent a class of nitrogen-rich POPs with highly tunable chemical composition and porosity that make them potentially valuable candidates for gas capture/storage and for application in catalysis [1].

In this study, 1,3-dicyanobenzene and 2,6-dicyanopyridine are selected as the starting building blocks for the synthesis of CTFs at various temperatures (Scheme 1). The adopted synthetic conditions along with the selected dicyano-precursor, allow to tune the final materials porosity and N-content. The as-prepared CTF samples are completely characterized before being successfully used as metal-free systems for: a) the steam-free direct dehydrogenation (DDH) of ethylbenzene into styrene and b) the selective and highly efficient adsorption of CO_2 and H_2. We have demonstrated, for the first time, that CTFs are valuable candidates to promote DDH efficiently, outperforming the industrial benchmark K-Fe catalyst and ranking among the best catalytic metal-free systems reported so far [2]. Notably, chemically accessible surface basicity as a key factor for the inhibition of the catalyst deactivation has been unveiled for the first time. Finally, these high-surface area and N-rich materials have demonstrated unique features for H_2 storage and CO_2 capture and sequestration [3].



Scheme 1

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OR-49

Single cell electrochemiluminescence imaging: from the proof-of-concept to disposable device-based analysis

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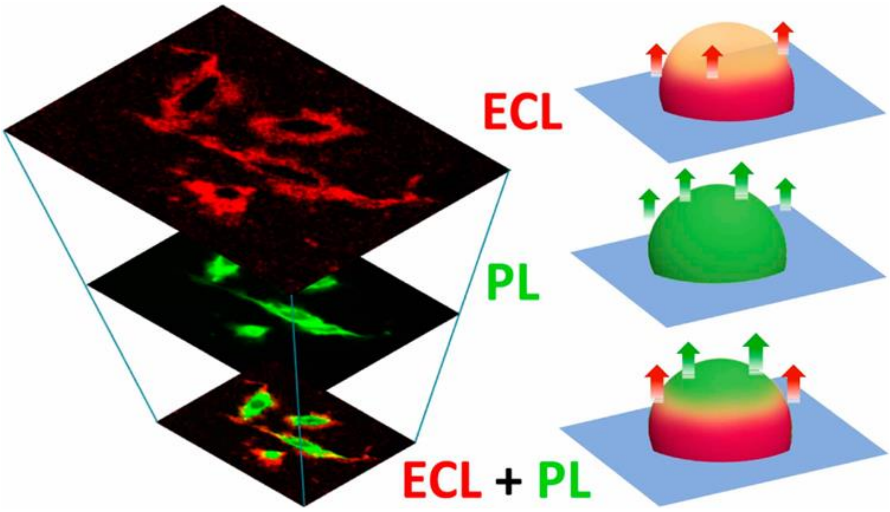
Electrochemiluminescence (ECL) is a leading technique in bioanalysis [1]. Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence. These properties make ECL systems particularly attractive also for microscopy imaging techniques [2].

Here we present the application of optically transparent electrodes based on carbon nanotubes materials to ECL, demonstrating the electrocatalytic superiority of such materials vis-à-vis ITO electrodes. The employ of carbon nanotubes resulted in a ten times higher emission efficiency compared to commercial transparent ITO electrodes.

Finally, we present the potential diagnostic applications of our approach thought the direct ECL imaging of overexpressed proteins on tumor cells [3].



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OR-50

Structural optimization, *in vitro* characterization and *in silico* pharmacophore modeling of a new antiplasmodial chemotype

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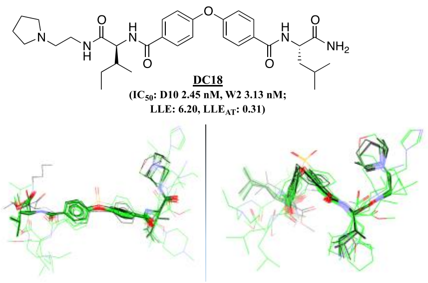
Malaria is the most common parasitic disease worldwide, and the third deadliest infection after HIV and tuberculosis. Due to the risk of diffusion of artemisinin resistance in Africa, new drugs for ensuring efficacious antimalarial treatment are urgently needed. In one of our previous communications, we reported the discovery of a new 4,4′-oxybis benzoic acid-based chemotype with promising antimalarial activity against both CQ-sensitive and CQ-resistant *P. falciparum (Pf)* strains. The IC_{50} were in the low nM range [1].

Here, we present our exploration of the structural requirements for the inhibition of *Pf* growth by this new chemotype through a detailed SAR investigation focused, also, on the improvement of its drug-likeness parameters. Our investigation led to the identification of the potent antiplasmodial compound **DC18**.

DC18 was deeply investigated *in vitro*: assays against gametocytes as transmission blocking agent, either alone or in association, its activity in the liver stage and ability to induce hemolysis and cytotoxicity on human cells are among the topics that were verified and studied.

Furthermore, an *in silico* analysis was run to build a pharmacophore model for this new, still target-less, antiplasmodial chemotype.



DC18
(IC$_{50}$: D10 2.45 nM, W2 3.13 nM;
LLE: 6.20, LLE$_{AT}$: 0.31)

Figure 1. The structure of *DC18* (up) and its ligand overlay-based pharmacophore modeling (down).

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OR-51

Aggregation paths of poly-3-(hexyl thiophene) in the presence of either PCBM or poly(ε-caprolactone)

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Poly-3-(hexyl thiophene) (P3HT) is currently the benchmark semiconducting polymer for organic photovoltaics. Its physical, electrical, photophysical properties are strongly dependent on its morphology in the solid state. However, several issues remain unclear, regarding the forces that drive the assembly/crystallization of P3HT to form fibrillar nanocrystals (NCs) in marginal solvent conditions (anisole) [1,2].

This work reports the results of a systematic study on the aggregation/crystallization behavior of P3HT to NCs under different solution conditions and in the presence of different relative contents of either PCBM [3] or poly(ε-caprolactone) PCL. PCBM and PCL confined the aggregation/crystallization process of P3HT NCs allowing the formation of extended crystallites, on the other hand at high concentrations in solution it hindered the formation of NCs slowing down their assembly. The results obtained in this work offer a promising perspective for the obtainment of functional all-polymeric NCs.

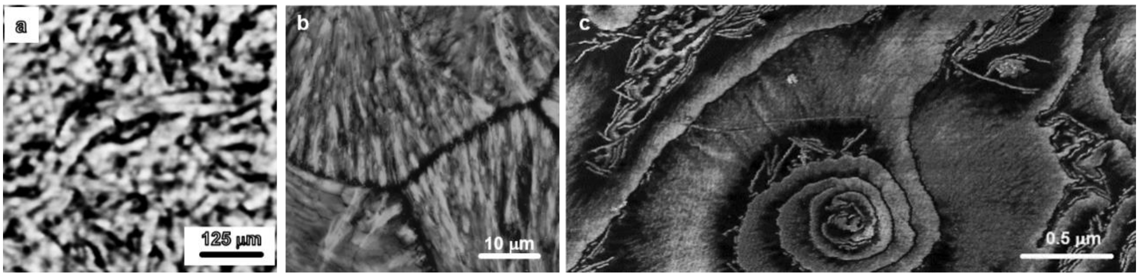

Figure 1. AFM phase micrograph of P3HT NCs mixture obtained from a) P3HT:PCBM 1:1, b) and c) P3HT:PCL 160:1 relative concentrations (w/w).

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OR-52

Dye-sensitized ethanol photoreforming for H_2 production

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Hydrogen is both a fundamental chemical and an almost ideal energy carrier, because it has no carbon footprint and can be ideally obtained from photocatalytic water splitting. Despite that, the low efficiency of the latter process, due to the high oxidation potential required for the water oxidation reaction, hampered its application on a large scale [1]. A possible way to overcome this drawback is the photoreforming of renewable feedstocks, in which a sacrificial electron donor (SED), such as an organic molecule, is necessary for the H_2 production.

In our recent work [2], we sensitized Pt/TiO_2 nanoparticles with several rationally designed organic donor-acceptor dyes (figure 1) and employed them as photocatalysts for the H_2 production in the presence of both triethanolamine and, for the first time, ethanol as SEDs. The synthesis, characterization and catalytic activity of all the dyes will be presented in this communication.

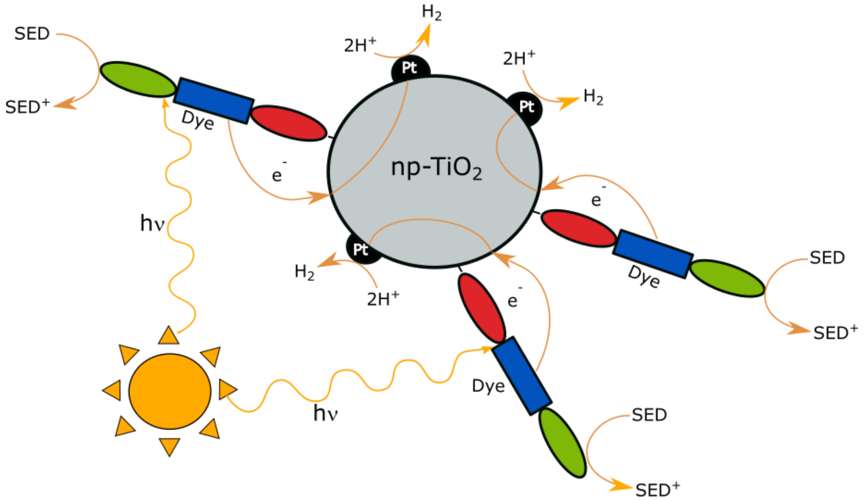

Figure 1: Mechanism of photocatalytic H_2 production.

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OR-53

Rational control of the activity of Cu^{2+}-dependent DNAzyme by re-engineering purely entropic disordered domains

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Here we modulate the catalytic activity of a Cu^{2+}-dependent self-cleavable DNAzyme by rationally introducing different intrinsically disordered regions that, through a purely entropic contribution, control the folding, and thus activity, of the DNAzyme.

To do this, we have designed a triplex-forming DNA sequence that, by recognizing a 11-base DNA strand through the formation of a clamp-like structure, folds into the highly conserved catalytic core of the Cu^{2+}-dependent self-cleavable DNAzyme. The affinity with which the triplex-forming DNA sequence binds to the 11-base DNA strand can be modulated by varying the length, and thus the entropy, of the loop that connects its two recognition portions (Figure 1). This allows to modulate the catalytic activity of the Cu^{2+}-dependent self-cleavable DNAzyme through a simple modulation of the entropy associated to its folding in a very versatile and precise way [1,2].

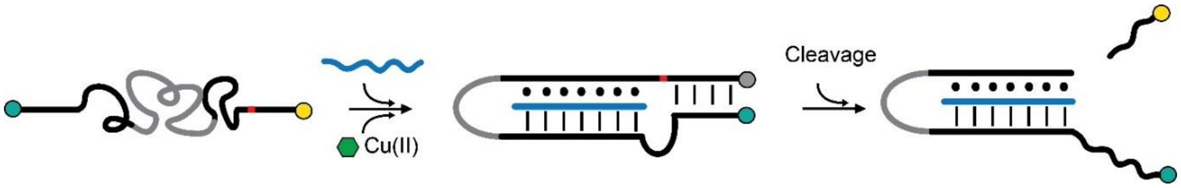

Figure 1. Triplex-forming Cu^{2+}-dependent self-cleavable DNAzyme.

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OR-54

Drug delivery system based on carbon nanotubes: synthesis and biological essays

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The ability of carbon nanotubes (CNT) to penetrate the cell membrane, together with the flexibility of their functionalization chemistry, has promoted them as one of the most interesting platform for the design of a new class of nanomaterial-based Drug Delivery System (DDS) [1-3]. CNT have been used as carriers for many cytotoxic drugs, gene therapy agents, photodynamic and photothermal therapy [4]. Furthermore CNT possess structural characteristics, that allow the design of new DDS able to carry two, or more, bioactive compounds [5,6]. Such devices are being studied and revealed efficient in combined therapy studies. For example, CNT have been used in combined therapy studies as carriers for pairs of cytotoxic drugs, pairs of gene transfection agents and in many of the possible combination of bioactive agents that are used in classic clinical approaches. Here we report the synthesis and the study of a multimodal drug delivery system based on short oxidized multiwalled CNT. The drugs selected were doxorubicin, frequently reported as gold standard for the drug delivery ability study on CNT, and metformin, an approved drug in type B diabetes therapy, which was recently reported as antimetabolic drug for the treatment of chemo-resistant tumor. The biodistribution of the system was investigated in 4T1 tumor bearing mice using different radioactive tracers and different time point. To fully understand the in vivo behavior of our new material we also studied how different type of administration can affect its pharmacokinetic.

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OR-55

In vivo functionalization of diatom mesoporous biosilica for bone tissue engineering

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Bone desorption related disease such as osteoporosis, Paget's syndrome and bone tumours are one of the most frequent pathologies of industrialized countries [1]; for the treatment, osteoclast inhibitor bisphosphonates (BPs) are used to increase the bone matrix production. Unfortunately, bisphosphonate uptake presents several side effects such as osteonecrosis and cancer: therefore, a BP delivery *in situ*, in the damaged area, would reduce the administered drug amount and consequently the side effects. For this reason, bone filler mesoporous materials conjugated with drugs have been proposed [2].

Beyond the fabricated porous materials, in nature some organisms are able to produce highly porous shells: for examples, hierarchically organized mesoporous frustules are biosilica shells produced from diatoms microalgae. Diatoms are low cost source of porous biocompatible silica, with a variety of applications. In particular, it has already been shown how frustules can be easily conjugated to drug molecules [3]. In the lecture, we will briefly discuss about the possibility to functionalize mesoporous biosilica with sodium alendronate, a second generation bisphosphonate. In particular the drug was immobilized in the porous hierarchically organized biosilica shell of photosynthetic diatom microalgae simply by adding the organic molecule in the culture medium. FTIR, SEM-EDX and TGA analyses prove the *in vivo* functionalization of the shell. Then, the alendronate-frustule scaffold was tested on mammalian cells: osteoblast-like cell viability increase, while osteoclasts apoptotic bodies were obtained. This new generation material is a promising tool for tissue engineering.

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OR-56

Uranyl cation as visible-light photocatalyst for C-C bond formation via hydrogen atom transfer

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The use of photocatalytic reactions in organic chemistry has recently gained increasing attention due to the mild conditions involved and because they enable unconventional pathways in synthesis. These reactions are based on the use of a photocatalyst (**PC**), a species that is responsible for light absorption and, once in the excited state, for the activation of the substrates of the reaction through a *chemical* step. For example, photocatalyzed Hydrogen Atom Transfer (HAT) is a chemical process where an inert C-H bond is homolytically broken by the excited state of **PC** to afford fleeting intermediates, such as C-centered radicals, under mild conditions [1]. If, on one side, this might appear as the philosopher's stone for synthetic chemists, on the other this research field has known a frustrated growth, one of the main restrictions being the scarcity of catalysts compatible with cheap and versatile visible-light irradiation systems.

Recently, the fluorination of cycloalkanes and oxygenated compounds by means of the uranyl cation, in the form of its nitrate salt $[UO_2](NO_3)_2 \cdot 6H_2O$, was achieved under blue light irradiation. The reaction occurred via HAT [2]. Pushed by our interest in C-H to C-C bond conversion via HAT by polyoxometalates [3], where an M=O (M: metal) functionality in the excited state is responsible for the relevant H-atom abstraction, we studied the efficiency of the uranyl cation ($[UO_2]^{2+}$) under irradiation at 456 nm in this process. Remarkably, cycloalkanes, ethers, amides and acetals were functionalized with electrophilic styrenes in high yields according to the Giese reaction. Even though preliminary, our data are sound and the scope is currently being expanded with particular attention devoted to mechanistic aspects.

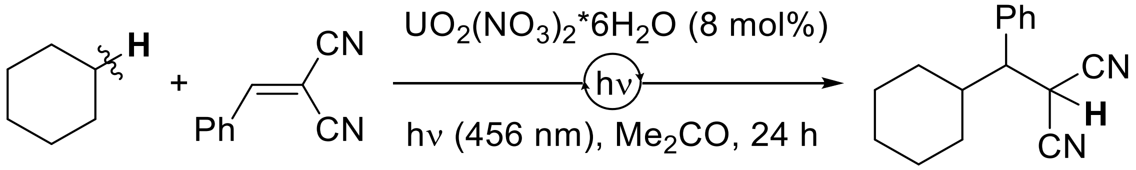

Figure 1: Uranyl cation as visible-light photocatalyst for C-C bond formation via HAT.

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OR-57

A new synthesis of indolin-3-one derivatives

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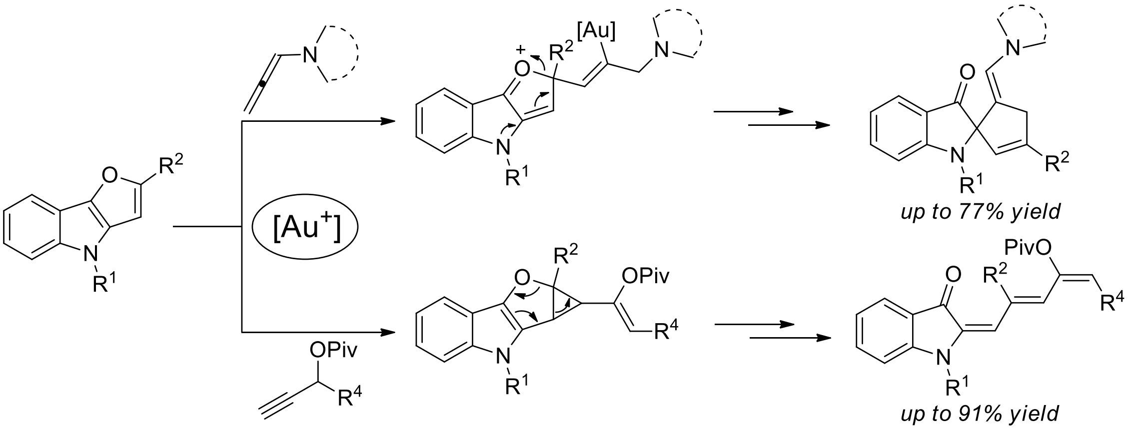
Indolin-3-one scaffold occur in the core structure of a large number of compounds with pharmaceutical and biological importance. In particular, 2-spirocyclopentane-indolin-3-ones are reported in literature as components of several alkaloids with interesting biological properties or as intermediates for the synthesis of active pharmaceutical compounds [1]. Moreover, they share with the corresponding 2-methylene-indolin-3-ones emergent applications as functional fluorescent dyes [2]. Taking into account these premises and our experiences in the transition metal catalyzed synthesis and functionalization of indole derivatives [3], we decided to explore the reactivity of 4*H*-furo[3,2-*b*]indoles in the presence of gold(I) activated □-systems for the synthesis of new classes of indolin-3-one derivatives. In particular, employing *N*-allenamides or propargylic esters, a careful screening of the gold(I) catalysts allowed for the synthesis of two different classes of indolin-3-ones through gold-promoted cascade sequences involving functionalization at the furan moiety followed by a ring-opening event, Scheme 1. The obtained results will be presented with particular focus on the optimization of catalytic reaction conditions and on reaction mechanism.



Scheme 1. Indolin-3-ones from 4H-furo[3,2-b]indole under gold(I) catalysis.

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OR-58

Chiral aggregation of ZnTPPS on polylysine: chain length effects

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Over the last decades a fascinating development in chemistry is the construction of nanomaterials from small building blocks by self-assembly.

In this respect, porphyrins represent ideal organic building blocks for the formulation of functional supramolecular materials. They own topological diversity as well as minimal conformational flexibility. Moreover, they are steady under a large variety of conditions, and can be readily fine-tuned to self-organize in predefined supramolecular architectures [1].

However, one of the most relevant issues associated to supramolecular chemistry is to gain the control of self-assembly processes in aqueous solution in order to create functional materials designed for specific applications.

Polyelectrolytes are often used to promote aggregation of porphyrins through electrostatic driven self-assembly, assisted also by dispersive forces [2].

Herein, we demonstrate that the poly-L-lysine (PLL) chain length influences, at acidic condition, the demetallation rate of zinc(II) meso-tetrakis-(4-sulfonatophenyl) porphyrin (ZnTPPS) affecting the chirality of J-aggregates formed after protonation of the porphyrin. Spectroscopic investigations evidence how longer PLLs promote structural reorganizations of the protonated porphyrins leading to the formation of ordered J-aggregates [3].

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OR-59

Total synthesis of a triazole analogue of Ixabepilone

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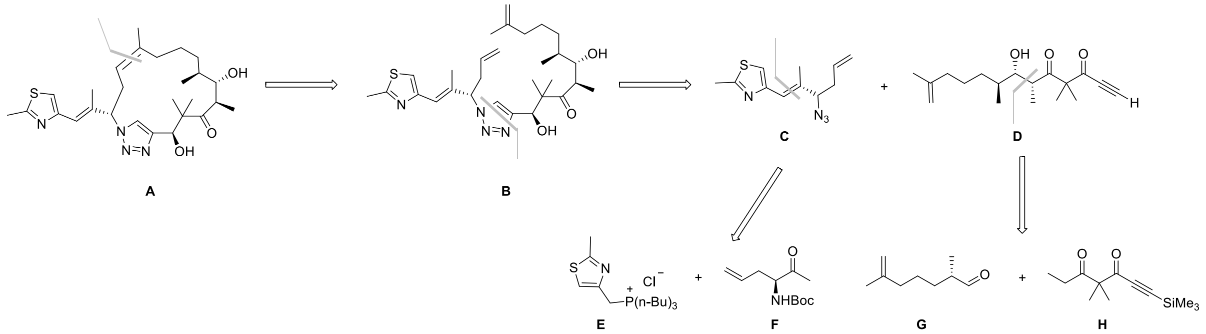
Analogues synthesis is one of the most used strategies for the improvement of pharmacokinetic properties of existing active molecules, solving problems such as poor solubility or poor cellular uptake, which limit their therapeutic applications. In these cases, the substitution of some functional groups allows the obtainment of more active compounds and the identification of the structural features of the pharmacophore.

Following our interest in bioisosteric substitution of amide bonds with 1,2,3-triazoles, attested by the synthesis of triazole active analogues of different anticancer drugs as Imatinib, Triflorcas, Vismodegib [1, 2], and of an already existing active analogue of Migrastatine [3] with very promising results, we approached the total synthesis of an analogue of Ixabepilone, an anticancer drug belonging to epothilones family.

In this comnmunication we report our efforts to obtain the analogue (Scheme 1).



Scheme 1. Retrosynthetic pathway of Ixabepilone triazole analogue.

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OR-60

NHC-catalyzed external oxidative desymmetrization of pharmaceutically relevant dihydropyridines

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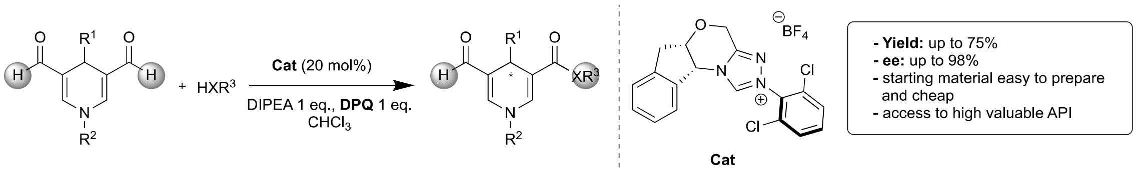

The synthesis of 1,4-dihydropyridines (DHPs) was first published by A. Hantzsch in 1882 via a multicomponent approach [1]. About 60 years later compounds of this class were found to exhibit pharmacological activities as analgesic, morphine agonist and antispasmodic and in 1975 they became the most important drugs used in the treatment of cardiovascular diseases when nifedipine (Adalat®) appeared on the market for the first time [2].

More recently, NHC (N-Heterocyclic Carbene) catalysis has emerged as powerful tool in desymmetrization and resolution of alcohols via external and internal oxidation of Breslow intermediate [3]. Thus, we envisioned the possibility to extend this approach directly to symmetric dialdehydes.

Herein, we present a strategy for the synthesis of biologically relevant DHPs with high optical purity via NHC-catalyzed desymmetrization of 1,4-dihydropyridine-3,5-dicarbaldehyde. The Kharasch oxidant (DPQ) was found to be the best external oxidant in the process and a small library (18 entries) of DHPs was prepared. The reaction is robust and proceeds with good yield (up to 75%) and excellent enantioselectivity (up to 98%). Some synthetic elaboration of the compounds are presented as well.

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OR-61

Fmoc-FF and hexapeptides-based multicomponent hydrogels as scaffold materials

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Peptide-based materials represent a rapidly growing tool within materials science. They have been considered for several applications. Short peptides are interesting building blocks for hydrogels fabrication, used as extracellular matrix-mimicking scaffolds for cell growth in tissue engineering. The combination of two or more peptide hydrogelators could allow the obtaining of hybrid materials. Here we report on the formulation and multi-scale characterization of novel peptide-based mixed hydrogels formed by the low molecular weight hydrogelator Fmoc-FF (N$^{\alpha}$-fluorenylmethyloxycarbonyl diphenylalanine) [1] and of the PEG$_8$-(FY)3 hexapeptide, containing three repetitions of Phe-Tyr motif and a PEG moiety at its N-terminus [2]. Mixed hydrogels were also prepared replacing PEG$_8$-(FY)3 with its analogue (FY)3, without the PEG moiety. Rheology analysis confirmed the improved mechanical features of the multicomponent gels prepared at two different ratios (2/1 or 1/1, v/v). The capability of these hydrogels to encapsulate doxorubicin (DOX) as drug model was checked. Preliminary *in vitro* biocompatibility and cell adhesion assays performed on Chinese Hamster Ovarian (CHO) suggest a potential employ of these multicomponent hydrogels as exogenous hybrid scaffold materials.

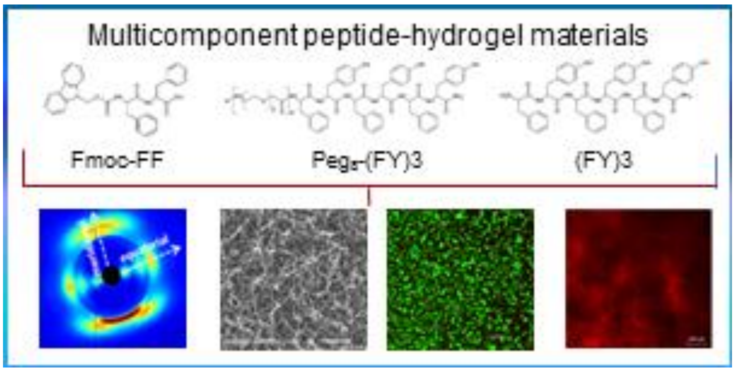

Figure 1. Peptide components of novel hydrogels.

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OR-62

“Inherently chiral” ionic-liquid media: effective chiral electroanalysis on achiral electrodes

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Chiral electroanalysis could be regarded as the highest recognition degree in electrochemical sensing. A groundbreaking strategy was recently proposed, based on the use of "inherently chiral" molecular selectors, *i.e.* with chirality and key functional properties originating from the same structural element.

Large differences in peak potentials have been observed for the enantiomers of different chiral probes: *(a)* working on inherently chiral electrode surfaces consisting of thin oligomer films [1] electrodeposited from enantiopure inherently chiral monomers; *(b)* working on achiral electrodes, implementing inherent chirality in their interphase with an ionic liquid medium [2] exploiting the latter's peculiarly high order. Inherently chiral ionic liquids, ICILs, were developed as double salts of an atropisomeric 3,3′-bipyridine scaffold with long alkyl chains and a suitable anion. Even more convenient, the new ICILs as well as other family terms solid at room temperature but of easier synthesis, or other inherently chiral salts, can be efficiently applied as low-concentration chiral additives in commercial achiral ionic liquids: large peak potential differences, regularly increasing with additive concentration, have been observed for the enantiomers of different probes on achiral electrodes.

The inherent chirality research is currently supported by Regione Lombardia and Fondazione Cariplo (Project 2016-0923).

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OR-63

X-ray structure and ionic conductivity study of choline-chloride/carboxylic acid DESs

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The quest for sustainable chemistry is fortunately an unstoppable process, and a new class of biodegradable compounds, the Deep Eutectic Solvents (DES) [1], has recently been proposed as inexpensive and "greener" alternative to ionic liquids. Such a new class is composed of eutectic mixture of solids, usually the quaternary ammonium salt choline chloride, and a hydrogen-donor (HBD) Brønsted base, where the extensive charge delocalization resulting from the interactions between the anion and the non-symmetrical HBD moiety is responsible for the very large decrease of the mixture solidification temperature compared to the single components. Though DES share most of ionic liquids physical properties, like negligible vapor pressure, ionic conductivity, high solvating power for a wide variety of substances, they are chemically distinct from conventional cation–anion paired IL, since their being in the liquid state depends largely on the molar fractions of the mixtures. Furthermore, most DES are inherently atoxic, since their components are benign molecules obtained from natural sources [2].

Despite the undeniable value of these compounds, their structures and structure-property relations have not been fully characterized yet [3]. In this study, we report the density, viscosity and structure of some choline chloride—carboxylic acid mixtures, using, for the first time, the Energy Dispersive variant of X-Ray Diffraction (EDXD), and interpret experimental data with molecular dynamics simulations. The effect of water content in the DES is also investigated.

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OR-64

Crosslinked poly(ethylene oxide)-based polymer electrolytes for advanced Li-ion batteries

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Self-standing and tack-free ethylene oxide based polymer electrolytes with improved ionic conductivity are successfully prepared via a rapid and easily up-scalable UV/thermal curing process. Free radical polymerization (UV/thermal-curing) can be an interesting alternative to produce polymer electrolytes, being highly advantageous due to easy and fast processing, high efficiency and eco-friendliness as the use of solvent is avoided. All of the prepared materials are characterised in terms of physico-chemical, morphological and electrochemical properties.

The crosslinking produced during curing allows the incorporation of high amount of RTIL (e.g., with imidazolium and pyrrolidinium cations) or tetraglyme and lithium salt ($TFSI^-$ anion), leading to a material with remarkable homogeneity and robustness. The polymer network can efficiently hold plasticizers without leakage. Samples are thermally stable up to 375 °C under inert conditions, which is particularly interesting for application in Li-ion batteries with increased safety. Excellent ionic conductivity (>0.1 mS cm−1 at 25 °C), wide electrochemical stability (> 5 V vs. Li), stable interfacial properties and dendrite nucleation/growth resistance are obtained. The lab-scale Li-polymer cells assembled with different electrode materials (e.g., $LiFePO_4$, Li-rich NMC, TiO_2) show stable charge/discharge characteristics with limited capacity fading upon very long-term reversible cycling [1-3].

The overall remarkable performance of the novel polymer electrolytes postulates the possibility of effective implementation in the next generation of safe, durable and high energy density secondary Li-ion polymer batteries working at ambient and/or sub-ambient temperatures.

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OR-65

Graphite intercalation compounds as effective platforms for the preparation of highly active electrocatalysts toward oxygen reduction and evolution reactions

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The integration of carbon materials in appropriate nanostructures has been recognized as a very powerful approach to improve the performance of state-of-the-art catalytic materials [1]. Up to date, the vast majority of examples published on the generation of nanoparticles/graphene composites rely on surfactant/water-based dispersions of graphene or graphene oxide and the addition of metal salts as well as reducing agent to that dispersions.

Graphite intercalation compounds (GICs) can be readily exfoliated to monolayer graphene in organic solvents, and the resulting solutions are composed of charged graphene layers. The direct reaction of GICs with metal salts has advantages over the above-mentioned processes, as the reduction of the metal takes place in close proximity of the carbon lattice. This results in NPs with a unique distribution in size, and a preferential growth near the edges of the GICs [2].

We synthesized the iron oxides/nanocarbon (Fe(np)/nCs) composites exploiting the reactions between graphenide solutions and iron salts (Figure 1). The different graphenide solutions with varying size distributions resulted in composites composed of carbon layers covered by different sizes of iron oxide nanoparticles. The composites show high activities for the oxygen reduction and evolution reactions in basic solution.

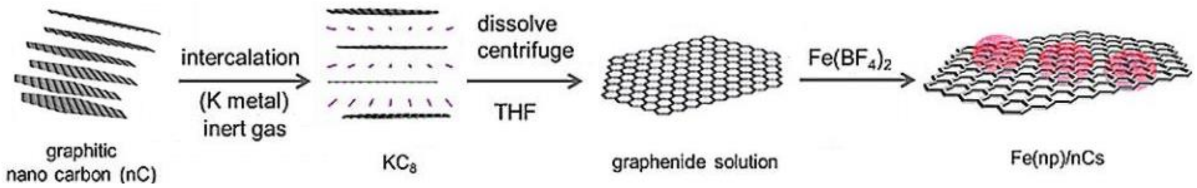

Figure 1. Reaction scheme for the synthesis of Fe(np)/nCs.

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OR-66

Preparation and characterization of zinc oxide based photoanodes for aqueous dye-sensitized solar cells

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This work focuses on the preparation and characterization of zinc oxide photoanodes conceived for water-based dye-sensitized solar cells (DSSCs). Nowadays, one of the main challenges is to replace the commonly used organic electrolyte solvents, which are highly volatile, hazardous and sensitive to moisture/water contaminations with water, the universal, greenest and cheapest solvent [1]. In this work, the redox couples were dissolved only in water and a biosourced jellifying agent, namely carboxymethylcellulose, was added to the electrolyte system to improve the long-term stability of the devices. In the framework of photoanode development, three different microstructures of ZnO with peculiar morphological characteristics were exploited to tailor the photoanode architecture, especially in terms of surface area of the semiconducting layer and electron transfer rate [2]. This target was reached with the desert rose morphology of ZnO. At the same time, the optimization of the sensitization conditions was carried out by means of a chemometric approach in order to limit/overcome the typical ZnO dissolution. Through this method the optimal manufacturing conditions were identified in 1 h of sensitization time and in a molar ratio of 1:50 between dye and co-adsorbent (chenodeoxycholic acid) concentrations in the sensitization solution; this led to an efficiency of 0.34% for lab-scale DSSCs (Figure 1).

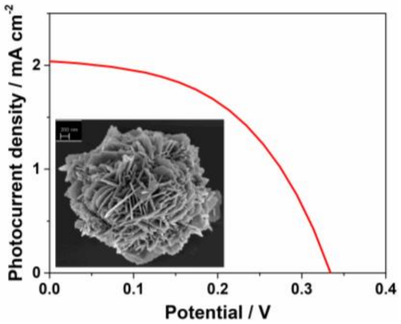

Figure 1: J-V curve of a DSSC prepared under optimized conditions. *Inset*: FESEM micrograph illustrating the peculiar desert rose morphology of ZnO.

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OR-67

Laminated silicon-graphene hetero-structure as high-rate anode for Li-ion batteries

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Silicon is one of the most promising candidate for the next generation Li-ion batteries. Silicon represents a feasible candidate for the next generation Li-ion batteries. The main advantages are related to high capacity values (≈4200 mAhg-1 for the fully lithiated alloy Li4.4Si) and low discharge potential (0,37 V vs. Li/Li+). Furthermore, it is abundant and non-toxic.

Unfortunately, many issues prevent its practical application in lithium devices. Specifically, lithiation/de-lithiation processes are associated with a large volume expansion-contraction changes (>300%) that can induce cracks and as consequence pulverization of the electrode, which eventually leads to rapid capacity fading in few cycles [1]. Reduction of silicon particles at nanometric level or their encapsulation in a carbonaceous matrix are some of the commonly adopted strategies to control the volumetric changes, reduce the lithium diffusion length and prevent the agglomeration of silicon particles, thus improving the performance of the electrode in terms of both life and rate capability [2]. In this context, graphene represents a suitable substrate to host active nanoparticles such as those of silicon, thanks to its unique chemical and physical properties such as high conductivity, mechanical flexibility and chemical stability [3].

In this communication, we report the development of a silicon-graphene composite and its investigation in terms of morphology and electrochemical performance, proving a low cost and scalable method to prepare such silicon-graphene composite, and achieving promising electrochemical performance in both half and full cell configurations.

Electrochemical tests in lithium cell proved that the composite achieves ≈2300 mAh/g with a Coulombic efficiency of 99% at a current density of 350 mA/g and over 1000 mAh/g at current values up 3.5 A/g.

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OR-68

Non-fluorinated ionomers and nanocomposite electrolytes for fuel cell applications: recent development and ions diffusion study

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The needs to design polymer electrolytes able to conjugate performance, durability and sustainable cost has induced a tremendous acceleration in the research devoted to the development of inexpensive and high-performing membrane materials both as competitive alternatives to commercial perfluorosulfonic acid membranes and with the objective of extending the range of operation of polymer fuel cells [1].

This talk will focus on non-fluorinated ionomers ensuring adequate devices' performances and reduced overall cost. Important requirements are satisfactory mechanical strength with respect to the levels of functionalization (generally sulfonation) as well as of hydration, allowing high proton conductivity and chemical stability in the aggressive environment of a working fuel cell. For this purpose, hybrid nanocomposites based on advanced nanostructured materials such as Layered Doubled Hydroxide and Nanoscale Ionic Materials (NIMs) are also taken into account.

An overview of the NMR methods to study the molecular dynamics in such kind of systems will be also provided. In fact, NMR is crucial to investigate not only the chemical structure but also the molecular dynamics, through the direct measurements of the self-diffusion coefficients and the relaxation times [2]. The ions diffusivity studies, together with electrochemical characterizations, as a function of T and RH, can allow to comprehend the relationship between architecture, dimensionality, chemical structure of polymers and nanofillers and the physicochemical properties of the resulting electrolytes.

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OR-69

Potentialities of hybrid nanocomposites based on RGO and Au NPs towards electroanalytical applications

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A novel "*in-situ*" synthesis of colloidal Au nanoparticles (Au NPs) anchored onto Reduced Graphene Oxide (RGO) flakes is presented. In particular, RGO is functionalized with 1-aminopyrene or 1-pyrene carboxylic acid, and the end functionalities of pyrene act as a heteronucleation and growing sites for the Au NPs, which have been synthesized with different sizes (ca. 2-3, 10 and 20 nm) and capping ligands (amine or thiol).

A deep electrochemical characterization of the as prepared hybrid nanocomposites has been performed, focusing on the role played by the single components, by means of Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements.

Synergistic effects, yielding to the enhancement of the system electroanalytical properties, are highlighted. The key point to understand the peculiarities of these innovative materials is the charge transfer from the Au NPs to RGO, assisted by the pyrene linker. These nanocomposites were applied in electroanalytical sensors for the detection of both organic and inorganic target molecules, such as As, dopamine and H_2O_2. In particular, in the case of dopamine, a LOD of (0.46 ± 0.02) ppb has been reached, comparable with other electroanalytical results of literature and in accordance with the benchmark for this molecule [1, 2]. For As detection, appropriately adjusting the experimental conditions, the hybrid devices show increased performances, also allowing speciation between As(III) and (V). In the case of H_2O_2, the hybrids platforms have been demonstrated ideal for developing oxidoreductase-based electrochemical biosensors, displaying high electrocatalytic activity and fast electron-transfer kinetics.

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OR-70

Advanced methodology for the characterization of early synthetic dyes used in cultural heritage using tlc and μ-enhanced spectroscopy

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AgI@Au TLC coupled to Enhanced Spectroscopies (MU-ATR-FTIR and SERS) was proposed as a highly sensitive methodology for the study of dyes extracted from fibers. Less than 0.01 mg of sample was analyzed avoiding the spectroscopic interference from fibers or other components. Different dyes commonly used in Cultural Heritage objects were tested and the method was validated on real samples dated back to 1893.

Enhance spectroscopies have become a useful tool to reduce the amount of sample when studying Cultural Heritage objects. In particular, MU-ATR spectroscopy has shown promising results for the analysis of dyes, same as SERS studies [1]. M2ADL group from the University of Bologna have proposed a methodology for the study of dyes micro extracts, which combines MU-ATR and SERS after separation by means of an ad hoc proposed AgI TLC plate.

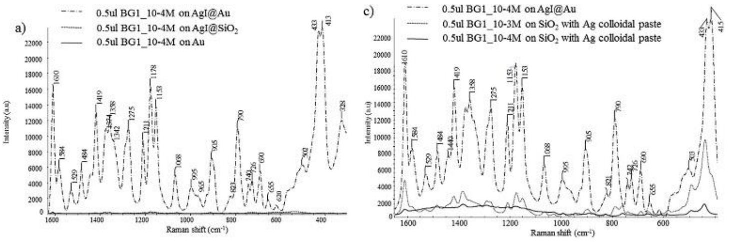

Figure 1. Spectra of BG1 extracted dye from wool with SERS and MU-FTIR-ATR after TLC development.

Dye standard solutions were preliminary analyzed on AgI@Au supports to understand the new plates capability to enhance FTIR and Raman signals. The method was tested for the identification of different acid and basic dyes extracted from dyed wool fibers artificially aged. The TLC separation allowed the elimination of interference from fibers and other components such as mordant. It was possible to identify dye even in degraded stages. The method was validated by studying real samples dated back from 1893. The combination of TLC, μ-MU-ATR, and μ-SERS result to be effective in the entire field in which analyses of a mixture of compounds present in trace amount are required.

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OR-71

Silica based matrices for the controlled release of glyphosate in soils

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The increase in pesticide consumption, in particularly glyphosate, is causing considerable health and environmental concerns, due to possible carcinogenic effects. The spreading of glyphosate on the soil, is generally done by spray spreading and low volume nebulizers, which however have the disadvantage to considerably diffuse the pesticide in the surrounding environment. Additionally, the operator's exposure to the herbicide is not negligible.

Based on the above-mentioned considerations, in this work the evaluation of time-controlled adsorption and release capacities of selected silica materials, characterized by low environmental impact, was studied. Four substrates, namely SBA-15, γ-alumina, montmorillonite K-10 (MMT K-10) and Al pillared montmorillonite (MMT-Al), were impregnated by incipient wetness impregnation technique, to obtain a 40% w/w of glyphosate inside each material. Release studies were performed, in aqueous matrices of different composition. Release yields were evaluated by using ion chromatography coupled with conductivity detection, at specific times (30,60 secs, 2,5,10,30, 60 mins, 24,48 hours, 3,5 and 7 days).

All tested materials, completely released the glyphosate within 30 minutes, except MMT-Al which exhibited a slow-releasing mechanism. In fact, both at acidic pH and in $CaCl_2$ solution, the herbicide is not completely released even after 2 days of contact. Analytical results were supported by physicochemical measurements, such as surface area and pore volume. The low pore volume value of MMT-Al (0.257 m^3/g), in fact, prevent diffusion of glyphosate during the releasing step, explaining the slow release kinetics. Furthermore, acid-base interactions could occur between the herbicide and Al atoms, which have an amphoteric behavior, thus giving them the possibility to act as Lewis bases. Kinetic models for controlled-releasing processes were also evaluated for MMT-Al, and pseudo first and pseudo-second order kinetics were found, depending on the composition of the receiving solution. Finally, post-release characterizations were also performed, suggesting that MMT-Al is not modified during the releasing process.

OR-72

QSAR models for the screening, prediction and refinement of PBT properties of contaminant of emerging concern

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Contaminants of Emerging Concern (CEC) represent a challenge for regulatory agencies that seek to protect the environment and human health from the potential harmful effects. Regulatory frameworks aim to ensure high level of health and environmental protection through the identification of the intrinsic properties of hazardous chemicals. Particularly relevant in screening assessments are the substances classified as Persistent, Bioaccumulative and Toxic (PBT) due to the potential risk they pose to human's health and ecosystems.

In this study the potential PBT behaviour of pharmaceuticals predicted by models based on Quantitative Structure Activity Relationship (QSAR) are used to draft a priority list of the most environmentally hazardous pharmaceuticals.

In addition, two integrated approaches are applied for the refinement of the Bioaccumulation and Toxicity assessment. In particular QSAR models to estimate the acute toxicity of pharmaceuticals in species at different aquatic trophic levels are developed and applied to prioritize pharmaceuticals and to refine the toxicity assessment of PBT screening.

Moreover, QSAR models for the prediction of *in-vivo* whole-body human biotransformation half-lives are developed for organic chemicals. These QSARs are used to predict the biotransformation potential of pharmaceuticals to refine the B evaluation of the previous PBT assessment [1].

Finally, predictions for the biotransformation half-lives are integrated into a mechanistic mass-balance multimedia environmental fate and exposure model to estimate the Biomagnification Factor (BMF) in humans for more than 10,000 organic chemicals as part of a tiered approach for B assessment in air-breathing organisms.

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OR-73

Mechanisms controlling P retention during Fe(II) oxidative coprecipitation

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The sorption of organic phosphorus (P) on soil minerals is known to strongly influence P cycling and control not only its availability to plants but also its transfer to waterbodies with consequent eutrophication. Considering the high affinity of Fe (oxy)hydroxides for P, the cycling of these two elements is often closely coupled, particularly in soils subjected to alternate redox conditions. This leads to the formation of negatively charged nanoparticles enriched in inositol phosphates with respect to more labile P monoesters and diesters. While surface adsorption has been widely studied, less attention had been devoted to the understanding of Fe-organic P coprecipitation, although it may affect the extent, kinetics and mechanisms of retention of various P forms.

In this work we synthesized Fe-P systems with increasing P/Fe ratio by either surface adsorption on ferrihydrite (Fh) or oxidative coprecipitation of Fe(II) with inositol hexaphosphate (IHP), phosphatidylcholine (PC) or inorganic phosphate (Pi) as control.

Coprecipitation resulted in a higher P retention with respect to adsorption. The presence of Pi reduced the rate of Fe precipitation with respect to the P-free system, resulting in nanoparticles with phosphate concentrated on the surface. IHP accelerated the precipitation of Fe through the formation of Fe-IHP complexes, leading to coprecipitates bearing IHP within the structure. The prevailing mechanism involved in PC interaction with Fe was instead physical retention. Irrespective of the P/Fe ratio, PC did not influence the rate of Fe(II) oxidation and precipitation.

Coprecipitation is therefore a more complex process than simple formation of a Fe(III)-hydroxide coupled with ion adsorption: several mechanisms can occur during Fe(II) oxidation, depending on the initial P/Fe ratio and P species. These results show the important contribution of this process to the stabilization and selective accumulation of IHP with respect to other P forms with important implications on its bioavailability and mobility towards waters.

OR-74

A novel NO-photoresponsive polymeric platform as an enhancer of doxorubicin delivery

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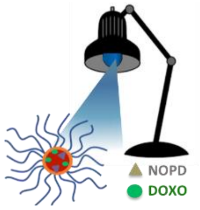
Nitric oxide (NO) is an endogenous messenger involved in cancer biology, low levels (pM-nM) of NO promote cancer growth, while high levels (μM) reduce cancer progression. The photogeneration of NO achieved using NO photodonors (NOPDs), namely, compounds able to release NO under the action of the visible light, has received a great attention as potential new anticancer therapy. Although the NOPDs studied by us [1,2], showed to release enough NO to perform an anticancer activity, with the purpose of further increasing its performance, a novel NO-photoresponsive polymeric platform as an enhancer of doxorubicin delivery was developed. An amphiphilic block-copolymers has been designed and synthesized as the drug carrier, via Ring-Opening Polymerization (ROP), and thoroughly characterized. The amine groups present in this polymeric system enabled the introduction of doxorubicin and NOPD, via N,N′-disuccinimidyl carbonate (DSC) chemistry. Subsequently, the two grafted-polymers were formulated in nanoparticles by the means of solvent displacement technique. Comparing free doxorubicin, DOXO-nanoparticles and the mixed micelles (formed by the coprecipitation of NOPD-polymer and DOXO-polymer) both in dark and light conditions, a remarkable enhancement in killing activity against lung, intestine, and skin cancer cell lines was observed when the mixed micelles were tested. Furthermore, the intra-cell colocalization study of each nanoparticle formulation was carried out. The next step will be to clarify if the enhanced anticancer activity is derived by the co-administration of NOPD and doxorubicin or is given to a synergic effect between the DOXO-polymer and NOPD-polymer.



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OR-75

Interactions between negatively charged nanoparticles and phospholipid bilayers: insights from molecular dynamics simulations

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Nanoparticles (NPs) are raising increasing interest in biomedicine, where they can be used as diagnostic or therapeutic agents. It is crucial, then, to understand how NPs interact with the cell membrane, and how their surface functionalization can drive this interaction [1].

Here we focus on a model system, constituted by a hydrophobic NP functionalized by anionic groups, and look at the interaction of this model NP with a phospholipid (DPPC) bilayer. Our work is motivated by the experimental observation by Wang et al., who noticed that the adsorption of negatively charged NP onto the surface of phospholipid layer can restructure the local bilayer phase, promoting a shift from the fluid to the gel phase [2].

We model the NP surface at different levels of complexity: as a continuous charged plane, and with all-atom, united atom and coarse-grained resolutions. Our results show that the influence of the NP surface on the membrane structure can not be interpreted as a purely electrostatic effect. In order to observe an alteration of the membrane structure, in the direction of favoring more compact and ordered (gel-like) lipid phases and disfavoring the liquid phase, it is important to take into account the molecular detail of the NP surface and the presence of ions in solution.

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OR-76

Effect of *Lactobacillus* biosurfactant on hydrocortisone solubilization and skin permeation

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An interesting strategy to enhance drug permeation across the skin is the use of permeation enhancers, such as surfactants [1]. Biosurfactants are amphiphilic compounds, produced by microorganisms on their cell surface or secreted extracellularly [2]. As reported in Abruzzo et al., 2018 [3], a biosurfactant (BC9-Bs) produced by *Lactobacillus gasseri* BC9 showed high surface activity together with a low critical micelle concentration (CMC).

The aim of this study was to evaluate the effect of BC9-Bs on solubility and skin permeability of hydrocortisone (HC), a naturally occurring corticosteroid that has strong anti-inflammatory properties. First, cytotoxic activity of BC9-Bs was assessed on human and murine fibroblasts. BC9-Bs ability to form nanometric self-assembling aggregates at concentration higher than CMC was studied by Dynamic Light Scattering. Moreover, HC solubility in the presence of different BC9-Bs concentrations was investigated and compared to Tween 80, used as control. Finally, *in-vitro* permeation studies were performed in order to evaluate BC9-Bs capacity to promote drug diffusion through different membranes, e.g. acetate cellulose, biomimetic artificial barrier Permeapad™, and porcine full-thickness skin.

Results showed that BC9-Bs was not cytotoxic and can provide the formation of nanometric aggregates in the range of 180-200 nm. Interestingly, HC solubility and permeability were increased in the presence of BC9-Bs, as a consequence of drug-Bs interactions. Moreover, at concentration lower than CMC, BC9-Bs allowed the permeation of an higher amount of drug with respect to Tween 80. In conclusion, these results suggest that BC9-Bs could be used as possible pharmaceutical excipient for skin permeation enhancement of hydrocortisone.

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OR-77

Hit identification of novel p38α MAPK inhibitors by *in silico* approaches

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P38α mitogen-activated protein kinase (MAPK) represents a key factor in the regulation of pro-inflammatory signaling networks and in the biosynthesis of cytokines [1]. Even though numbers of efforts have been focused on the discovery and development of new p38α MAPK inhibitors, no drugs targeting this protein are currently on the market. Thus, the identification of novel inhibitors of this target still represents an exciting area of research.

Against this backdrop we have recently focused our attention on the identification of new chemotypes of p38α MAPK inhibitors.

Towards this aim, an in-depth analysis of available crystal structures of p38α MAPK in complex with ATP competitive inhibitors has been carried out, getting insights into both the impact of protein target conformations on ligand binding and the key inhibitor features [2].

In parallel, molecular docking simulations were carried to study the impact of the i) ATP binding site conformation, ii) presence of conserved water molecules, and iii) use of multiple proteins. A four-protein ensemble model was selected as the best performing protein model, able to both reproduce experimental binding mode of co-crystallized inhibitors and discriminate active molecules from compound libraries [3]; this model was thus selected to perform a virtual screening campaign of our proprietary chemical library.

Docking-based virtual screening, molecular dynamics simulations, and ADME profile predictions led to the identification of two new chemotypes of p38α MAPK inhibitors showing an encouraging low micromolar activity in a functional p38α inhibition assay. A first round of hit exploration by in silico strategies will be also herein reported.

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OR-78

Activated carbon adsorptive recovery of X-ray contrast agent in aqueous solution and adsorbent regeneration

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Adsorption-desorption technology is an efficient tool for recovery and concentration of valuable compounds from spent materials or industrial wastes [1]. Among X-ray contrast media, Iopamidol (Iop) is widely used in medical diagnosis and higher price nonionic compound, also classified as an emerging pollutant because of its persistence and low biodegradability [2]. The present investigation assesses the recovery of Iop using activated carbon (AC) by adsorption-desorption method in flow mode. Adsorption of Iop was studied onto powder ACs (PACs) and granular AC (GACs), and among coconut powder AC (CPAC) has the best adsorption performance. In addition, adsorption kinetic, isotherm, thermodynamic and mechanism in batch mode all were conducted to further understand adsorption process. With the aim to scaling up the adsorption process from a laboratory to an industrial application, the adsorption and desorption processes were studied in a semi-continuous flow system. Regeneration of the spent CPAC and recovery of Iop have been performed in different solvents. Iop has been very efficiently recovered with methanol over five cycles of adsorption-desorption in the flow system. Furthermore, CPAC samples were characterized by SEM, BET, DRIFT, XPS and TGA before and after adsorption-desorption process. The present study highlights the potential of the flow mode adsorption-desorption technology for Iop recovery from aqueous solutions and following CPAC recycling. These findings should open the doors to new successful applications in industrial wastewater treatments.

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OR-79

Novel naphtho- and anthraquinone derivatives as multi-functional ligands for the therapy of Alzheimer’s disease

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Alzheimer's disease (AD) is a degenerative disease characterized by a neuronal and synaptic loss of different neurotransmitter systems, in particular the cholinergic one, and also by the accumulation of aggregates of β-amyloid (Aβ) and hyperphosphorylated tau proteins.

Since current therapies offer only limited and temporary benefits to patients, new strategies have been formulated on the basis of current knowledge of complex nature of AD. One of the leading approaches is the design and synthesis of multi-target ligands which may be promising candidates able to target simultaneously two or more of the pathogenic processes of AD. On the pattern of the previously multi-target identified leads [1], which displayed the ability to inhibit one or both Cholinesterases and Aβ aggregation with similar potency, our efforts have concerned the design and synthesis of new naphtho- and anthraquinone derivatives connected through an appropriate linker to an aromatic or heteroaromatic ring (Figure 1). These hydrophobic features have been selected for a more efficient interaction with a sequence of aromatic aminoacids of Aβ, which is implicated in the initial phases of Aβ aggregation in soluble oligomers and fibrillary species [2]. These derivatives have been evaluated *in vitro* for their inhibitory activities against Aβ aggregation and Cholinesterases; interestingly, most of the them shared low micromolar IC_{50} values against Aβ and some of them also proved to inhibit AChE and BChE, thus fulfilling the fundamental requisite for a multi-target mechanism of action.

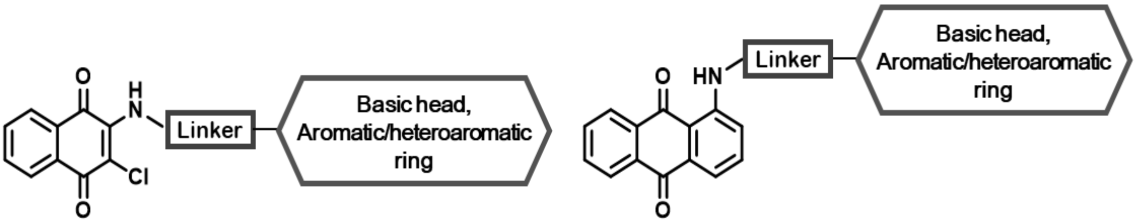

Figure 1. Scaffold of the investigated chemical classes.

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OR-80

Potent anti-glioblastoma agents by hybridizing an α7 nAChR antagonist and a mitocan

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Glioblastoma and adenocarcinoma cell lines overexpress α7 nicotinic acetylcholine receptors (nAChRs), whose activation promotes tumor growth.

On these cells, compound F1, a known selective antagonist of α7 nAChRs, has antiproliferative activity [1]. Compound RDM-4’BTPI, structurally related to F1, was reported to act as a mitocan by its inventors and therefore it exerts its antitumoral properties by enhancing reactive oxygen species (ROS) production in the mitochondria [2].

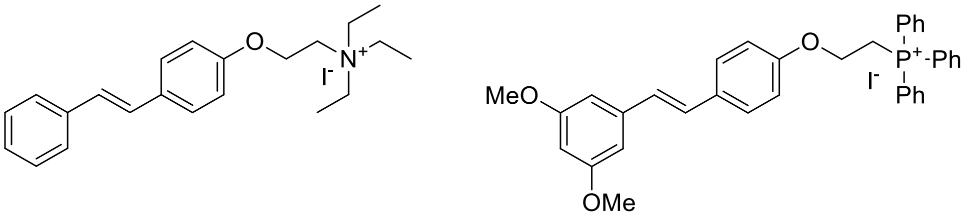

Figure 1. F1 (left) and RDM-4’BTPI (right).

Given the similar antiproliferative activities and structural similarities between F1 and RDM-4’BTPI, we aimed to understand whether their mechanisms of action (MoA) could overlap. Furthermore, we synthesized a series of hybrids between the two compounds, which were conceived to clarify which structural features drive the molecules toward two different MoA, and to obtain compounds with mixed and improved α7 antagonist/mitocan properties.

Upon proving that F1 could cross cell membranes, all the compounds were assayed for antitumoral activity at adenocarcinoma and glioblastoma cell lines. Binding affinities at the α7 subtype were measured for all the ligands and α7 antagonism was assayed for the most interesting ones. The mitochondrial functionality was evaluated both with a mitochondrial ROS production assay and an ATP production test.

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OR-81

A dual target kinase ligand as neuroprotective agent presenting two different mechanisms of enzymatic inhibition

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GSK-3β and CK-1δ are emerging targets for the treatment of neuroinflammatory disorders, including Parkinson's disease [1]. A dual inhibitor to target these two kinases was developed by docking-based design. Compound **12** (Figure 1) showed a balanced inhibitory activity against GSK-3β (IC_{50} = 0.17 μM) and CK-1δ (IC_{50} = 0.68 μM]. In particular, a classical ATP competition was observed against CK-1δ, and, for the first time, a co-crystal of compound **12** and GSK-3β confirmed a covalent interaction between the ligand and the Cys199 residue. The crystal structure could be a lead for the development of more potent covalent inhibitors towards GSK-3β. Preliminary studies on *in vitro* cellular models of Parkinson's disease revealed that compound **12** is not cytotoxic and shows neuroprotective activity. These results encourage new studies on GSK-3β/CK-1δ dual inhibition as a possible strategy to treat neuro-inflammatory/degenerative diseases.

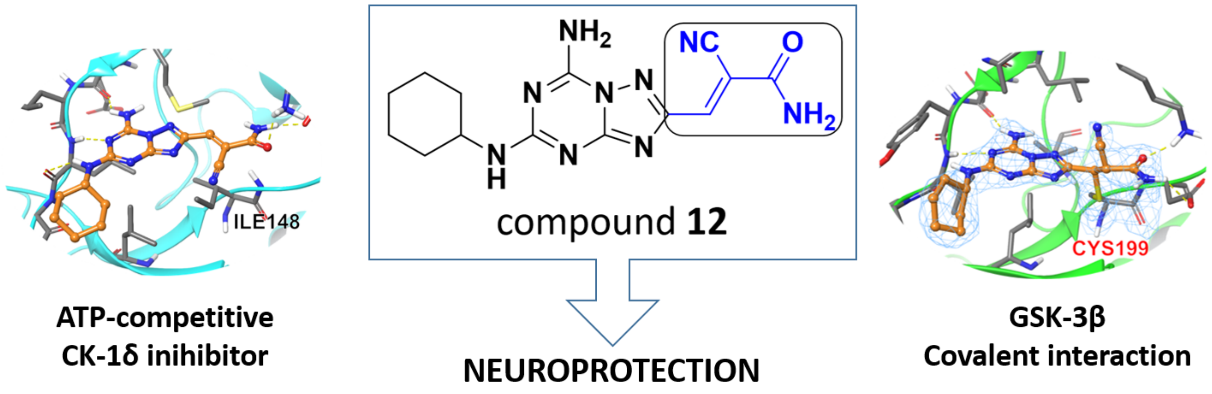

Figure 1

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OR-82

Potent and selective inhibition of Dengue e Zika viruses replication by pyridobenzothiazole compounds

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Recently, flaviviruses such as Dengue, Zika, and West Nile have emerged as life-threatening pathogens and neither drugs nor clinical candidates are available to treat these infections [1]. A promising antiviral approach is to target the NS5 RNA-dependent RNA polymerase (RdRp), which is an enzyme essential for viral replication without human analogue [2].

We recently reported the identification of the (pyridobenzotiazole)-4-carbonyltyrosine **HeE1-2Tyr** as new inhibitor of NS5 RdRp and of replication of Dengue and other flaviviruses [3]. A first round of SAR exploration focused on a ligand-based approach using **HeE1-2Tyr** as template led to a small series of C-4 modified derivatives and analogues derived from a core simplification. Biological evaluation of the new compounds highlighted a good inhibition of the isolate NS5 RdRp and potent and selective antiviral activity against Dengue and Zika replication in cells. Moreover, new important SAR information were obtained: i) the C-4 aminoacyl functionalization is essential for RdRp inhibition with the β-alanine and m-hydroxyphenyl alanine resulting as good replacers of the tyrosine side chain; ii) other non-aminoacidic substituents at the C-4 position are detrimental for NS5 RdRp inhibition but retain antiviral activity, iii) the pyridobenzothiazole core opening/size reduction is not tolerated for both target and virus inhibition. This survey led us to identify new promising anti-flavivirus compounds worthy of in vivo evaluation in Dengue virus infected mice.

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OR-83

ZINClick v.18: the 1,2,3-triazoles chemical space

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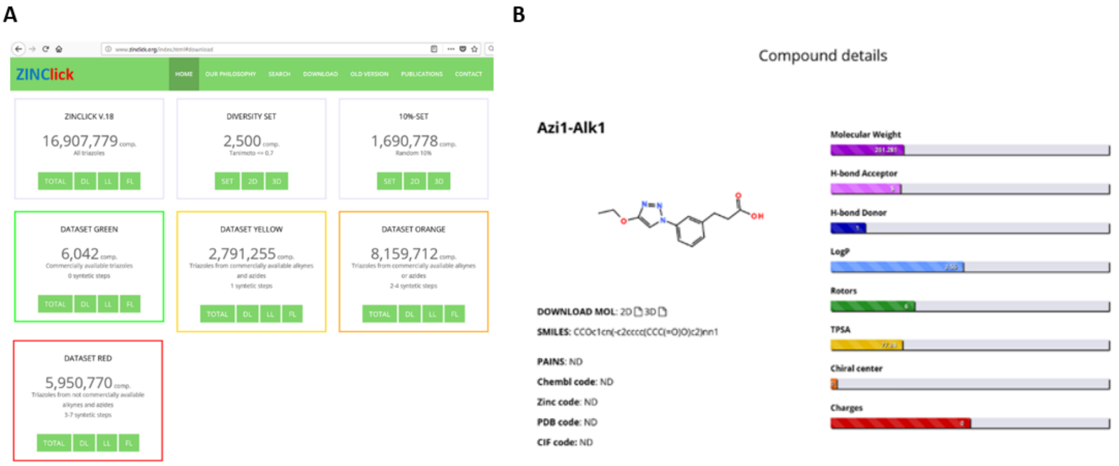
1,2,3-triazole scaffold is an attractive pharmacophoric group in medicinal chemistry. In fact, it is able to establish a wide range of interaction with biological target while maintaining a good pharmacokinetic profile [1].
In the last years, we have investigated the click-chemical space covered by molecules containing the triazole ring, we generated a database of 1,2,3-triazoles called ZINClick [2], starting from literature-reported alkynes and azides synthesizable in no more than three synthetic steps from commercially available products. This combinatorial database contains millions of 1,4-disubstituted-1,2,3-triazoles that are easily synthesizable, new and patentable. The library is regularly updated and it is freely downloadable (http://www.ZINClick.org). In this communication, the new implementation of ZINClick [3] will be discussed as well as our new strategy about clustering the chemical space covered by 1,4-disubstituted-1,2,3-triazoles around their availability: from direct purchase to different degree of synthetic feasibility of the compounds (Figure 1).



ZINCLICK V.18
16,907,779 comp.
All triazoles

DIVERSITY SET
2,500 comp.
Tanimoto <= 0.7

10%-SET
1,690,778 comp.
Random 10%

DATASET GREEN
6,042 comp.
Commercially available triazoles
0 syntetic steps

DATASET YELLOW
2,791,255 comp.
Triazoles from commercially available alkynes and azides
1 syntetic steps

DATASET ORANGE
8,159,712 comp.
Triazoles from commercially available alkynes or azides
2-4 syntetic steps

DATASET RED
5,950,770 comp.
Triazoles from not commercially available alkynes and azides
3-7 syntetic steps

Compound details

Azi1-Alk1

DOWNLOAD MOL: 2D 3D
SMILES: CCOc1cn(-c2cccc(CCC(=O)O)c2)nn1

PAINS: ND
Chembl code: ND
Zinc code: ND
PDB code: ND
CIF code: ND

Figure 1. Detailed view of the ZINClick v.18 webpage: (A) details of the subsets available to download, and (B) details page of a ZINClick triazole.

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OR-84

New *human* dihydroorotate dehydrogenase inhibitors able to restore myeloid differentiation in AML

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The success of brequinar, one of the most potent *human* dihydroorotate dehydrogenase (*h*DHODH) inhibitors, able to induce *in vitro* and *in vivo* myeloid differentiation in mouse acute myeloid leukaemia (AML) models [1], encourages researches to design new *h*DHODH inhibitors. By applying innovative scaffold-hopping replacement to brequinar, we designed a first generation of *h*DHODH inhibitors presenting nM activity [2].

In this occasion, we are presenting a second generation able to reach the brequinar *h*DHODH potency. Compound **1** was found also able to restore the myeloid differentiation in two leukaemia cell lines (U937 and THP-1) at concentrations one digit lower than brequinar. Theoretical design, modelling, synthesis, SAR, X-ray crystallographic data, biological assays, drug-like proprieties and in vivo toxicity are here presented and discussed.

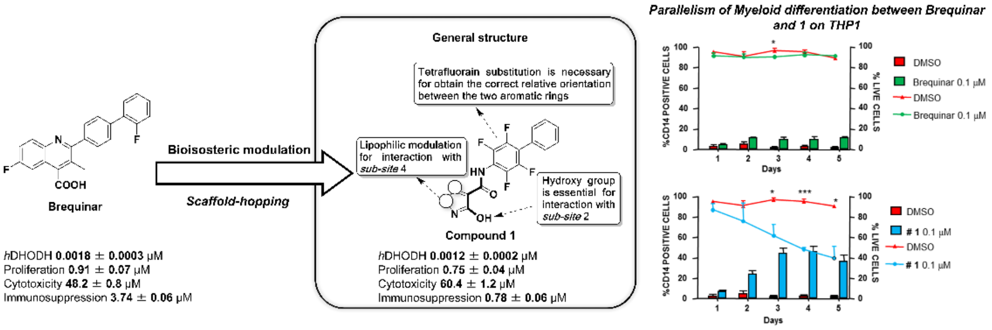

Figure 1. Brequinar structure and strategy for the design of compound **1**.

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OR-85

C-6/C-7 functionalization of the 3-phenylquinolone scaffold to obtain potent nontuberculous efflux inhibitors

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Antimicrobial resistance (AMR) is one of the most complex threat for human health and represents a hot topic in drug discovery.

Nontuberculous mycobacteria (NTM) are ubiquitous microbes belonging to *Mycobacterium* genus. Among all NTM pathogens, *M. avium* is one of the most frequent agents causing pulmonary disease, especially in immunocompromised individuals and cystic fibrosis patients. Treatment for *M. avium* infections consists of a macrolide, such as clarithromycin, for at least one year, but drug resistance associated to efflux pump (EP) activity often occurs [1]. Thus, identifying non-antibiotic molecules to inhibit the EPs could be a valid alternative to the discovery of new NTM antibacterials.

Given our previous proof that efflux pump inhibitors (EPIs) of the mostly studied *Staphylococcus aureus* also inhibit *M. avium* pumps [2], we recently improved EPI activity by synthesizing new 3-phenylquinolone derivatives as *M. avium* EPIs [3]. Unfortunately, all compounds suffered of significant cytotoxicity while showing a good EPI activity. Thus, in this work, we report the design, synthesis and biological evaluation of a panel of C-6 and C-7 functionalized 3-phenylquinolones. Most of them shows an improved CC_{50} value against human cells by maintaining or even increasing the EPI effect in synergism with a set of anti-mycobacterial agents against *M. smegmatis* and *M. avium* strains. Moreover, in order to prove that the synergistic effect is really due to EP inhibition, ethidium bromide efflux and accumulation assays have been performed against different NTM strains.

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OR-86

ZnO photocatalysts for enhanced CO_2 conversion

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Carbon dioxide photoreduction is an appealing way to both utilize CO_2 and sunlight as energy source. Despite the huge research in this field, CO_2 conversion by photocatalysis is still far from practical applications [1]. Titanium dioxide (TiO_2) is certainly the most studied wide-bandgap photocatalytic material, nevertheless zinc oxide (ZnO) is a promising alternative due to its lower charge carrier recombination rate [2]. In this ZnO catalysts were synthetized by a wet chemical method encompassing precipitation and annealing in air of the as-prepared material. A nanocomposite was also prepared, introducing TiO_2 as promoter on synthetized ZnO. The photocatalysts were tested on a lab-made gas-phase reaction rig with CO_2-H_2O gaseous reactants. Methane (CH_4) was the only observed CO_2 reduction product, moreover ZnO and TiO_2/ZnO exhibited a similar reactivity. Nevertheless oxygen formation, mainly arising from the poor ZnO photostability, was halved on the nanocomposite, due to a beneficial effect of TiO_2 [2]. Next, we assessed the recyclability of the best performing catalysts, namely the nanocomposite: no activity or selectivity losses were observed after two reuses and 18 hours of irradiation. Moreover, running the reaction with H_2O only we still observed CH_4, suggesting the CO_2 adsorbed directly from air can be reduced too. Concluding, in this work we synthetized ZnO-based photocatalysts by a mild technique. These materials exhibited a good selectivity and stability for CO_2 photoreduction; they also showed the remarkable capability of CO_2 conversion direct captured from air.

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OR-87

Exploring design rules in molecular electronics: the journey from design principles to functional materials

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The aim of molecular electronics is to make use of single molecules (or single molecular arrays) as active elements in the field of electronics [1]. Compared to silicon-based technologies, when dealing with entities on the nanometer scale, the quanto-mechanical nature of matter is relevant and might confer to the devices properties that are not possible to obtain otherwise.

One of the most studied examples of such behaviors is quantum interference (QI), which is a collection of phenomena related to Fermions whose wave functions can interfere with themselves [2].

In the case of molecular tunneling junctions, destructive QI can lower the transmission probability across the molecule by several orders of magnitude without altering the tunneling distance. Systems in which QI can be toggled on and off by external stimuli are of paramount interest to design devices that can show remarkable outputs on the molecular scale such as molecular switches, memories, and transistors.

Yet, to be able to translate these molecular properties in actual devices, it is not only necessary to understand the fundamental traits of QI but also to translate this knowledge to adequate design principles that can be used to achieve a better structure-function control oriented toward device fabrication.

In this study, we investigated (both theoretically and on different experimental platforms) the charge transport properties of a series of compounds characterized by identical molecular skeleton but different electronic structures, which are expected to give rise to QI. We found that electronic and collective effects can dominate simple structural considerations, thus opening the way to new approaches in the design of functional devices.

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OR-88

Microwave assisted synthesis of zirconia: solid catalyst for biomass valorisation

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Zirconia (ZrO_2) has been widely used for many technological applications, because of its interesting physical and chemical properties [1].

Microwave-assisted processing can help to overcome disadvantages of common synthesis techniques by reducing reaction time, improving yield and leading the preparation of a nanoparticles with homogenous distribution of both shape and dimensions [2]. We report a quick and green procedure to obtain zirconia based on a microwave-assisted sol-gel synthesis, followed by microwave-assisted calcination. The product obtained is almost tetragonal ZrO_2, as confirmed by different techniques.

ZrO_2-based catalysts can be employed in many different reactions as either simple metal oxide, as sulfated oxide or as support for metal catalysts, in particular in valorisation of lignocellulosic biomass. Using the same synthetic procedure, sulfated zirconia (SZ) and Nickel supported on SZ materials have been obtained that will be tested as catalysts in hydrolysis of lignocellulosic biomass to give levulinic acid and for biodiesel production.

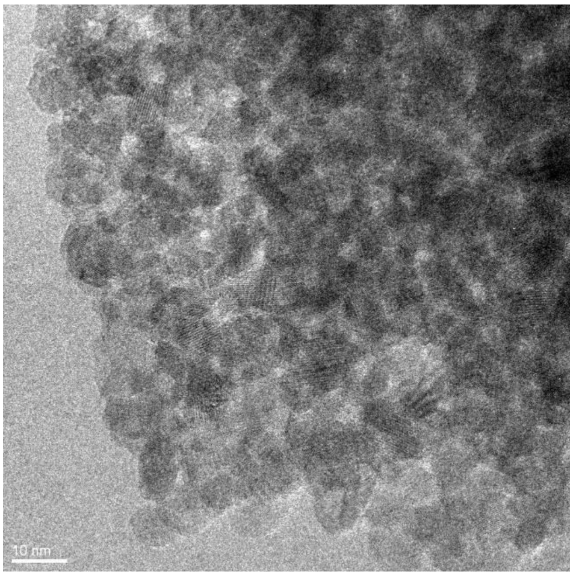

Figure 1. HR-TEM of zirconia nanoparticles.

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OR-89

Hydration of alkynes: homogeneous gold(I) catalysis in solvent and acid-free condition

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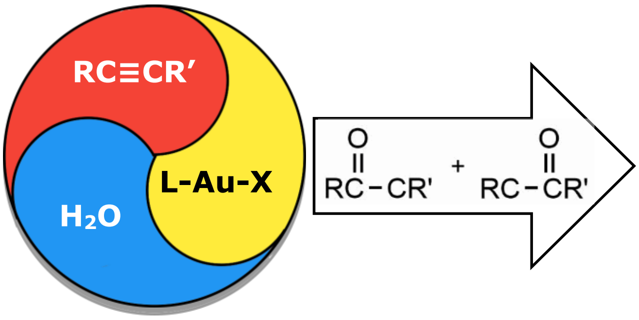
Engineering the reaction to reduce or eliminate the use or generation of hazardous substances in according to the twelve principles of the green chemistry, has become a must nowadays. The use of gold as catalyst in homogeneous catalysis often required unfavourable conditions due to the high temperature or the high amount of catalyst [1].

In this contribution, L-Au-X [L= 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene {NHC^{iPr}} tris(3,5-bis(trifluoromethyl)phenyl)phosphine {PArF}, bis(imino)acenaphtene-1,3-bis(2,6-di-isopropylphenyl)dihydroimidazol-2-ylidene {BIAN}, 1,3-bis(2,6-di-isopropyl-phenyl)dihydroimidazol-2-ylidene {NHC^{CH2}}, bis(*tert*-butylamino)methylidene {NAC}, 2-(di-*tert*-butylphosphino)biphenyl {JohnPhos}, tricyclohexylphosphine {PCy_3}, triphenylphosphine {PPh_3}, tris(2,4-di-*tert*-butylphenyl)phosphite {POR_3}, X^- = Cl^-, OTf^-, OTs^-] were tested as catalysts for the hydration of alkynes in neat and acid-free conditions, using tetra-butylammonium trifluoromethansolfonate as phase-transfer. The overall catalytic evidences confirm that not only the counterion, as previously observed by us [2], but also the ligand play a crucial role.

A complete rationalization of the ligand and counterion effects enabled us to develop a highly efficient methodology even for the hydration of inactive diphenylacetylene performing the catalysis in acid- and silver-free conditions with: low catalyst loading (0.01% with respect to the substrate), high TON (3400) and TOF (435 h^{-1}) at 120 °C, low E-factor (0.03), and high EMY (77).

- silver free
- acid free
- no solvent



- TON:3400
- TOF: 435 h^{-1}
- E_{factor}: 0.03
- EMY: 77

Figure 1. Gold(I) catalysis in net condition.

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OR-90

Molecular depth profiling by nitric oxide-assisted secondary ion mass spectrometry

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Sputtering of organic materials by high energy monoatomic primary beams causes profound rearrangements and modifications inside the sample, due to ion-beam induced “damage” processes. It is well known that, due to these processes, most of the chemical information in organic matter is lost and the in-depth information is limited to the elemental distribution only. Also, changes in density and sputtering yield can occur, introducing additional complications in data interpretation. Although, nowadays, most of the above issues have been overcame by the introduction of Giant Cluster Ion Beams (GCIBs), different approaches have been proposed, aiming to solve – at least partly – the problem of ion-induced chemical damage under monoatomic beam irradiation. In particular, Houssiau demonstrated the possibility of obtaining molecular depth profiles of polymers by using ultra-low energy Cs^+ ions [1], thanks to the inhibition of radical reactions by the reactive cesium accumulating at the sample surface. A similar inhibition process allows the improvement, by means of Nitric Oxide gas dosing, of C_{60}-based depth profiles of challenging polymers [2].

Although, presently, the performances of GCIBs for depth profiling of organics/polymers remain unparalleled, the use of “damaging” sputter beam conditions - in combination with processes that can partly inhibit the beam-induced chemical damage - can provide useful information about ion-beam induced reactions occurring during depth profiling, that are still largely unclear. Moreover, from the point of view of applications, the use of heavy monoatomic sputter beams could provide some advantage in terms of sputter yield uniformity and/or depth resolution in the case of hybrid samples.

In this context, we present some recent results on molecular depth profiling of polymers by NO-assisted sputtering with Cs ion beams with energy of a few keV. The effect of primary ion energy, NO partial pressure, polymer molecular weight and film thickness on the sputter yield and quality of depth profiles will be discussed.

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OR-91

Investigating photoelectrochemical properties of dye-semiconductor interfaces via a DFT-based embedding scheme

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Photoelectrochemical devices as Dye-Sensitized Solar Cells (DSSCs) are complex multicomponent systems in which the interfaces between different materials play a pivotal role. The treatment of such interfaces represents a challenge for state of the art computational tools. The simulation of photochemical processes on the dyes requires high levels of theory that are able to accurately treat excited states. On the other hand, a realistic modelling of the semiconductors (SC) nanoparticles forces us to increase the size of the system up to a scale where correlated wavefunctions (CW) methods are totally unaffordable. The standard computational approach for extended solid state systems is in fact Density Functional Theory (DFT), which is by construction only capable of treating ground state properties.

We propose a density functional-based embedding scheme to solve this incompatibility [1,2]. Embedding methods allow a partition of the system in two subsets: a cluster and an environment, the total energy being the sum of those from the two subsets plus an interaction term. This partition allows us to treat the cluster with high level methods while treating the SC with DFT. A potential term takes care of the interaction between the subsets.

Lots of works have been published on the development, implementation and testing of different embedding schemes. Most of these works focus on the performance of the methods applying them to some purpose-built models but very few use these methods to actually address problems of relevant chemical interest.

We apply the DFT-based embedding method to a recently studied system for p-type DSSC: a coumarine derivative dye adsorbed on p-type NiO [3], which is the current standard SC for these kinds of systems. We show how treating the dye with higher levels of theory, while treating the SC environment with DFT(+U) we can greatly improve the quality of the results obtaining information about the actual photochemistry of the dye.

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OR-92

Catalytic vs. electrocatalytic reduction of CO_2 to added-value products

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The increase of CO_2 concentration in the atmosphere after industrial revolution plays a critical role in global climate changes. Therefore, to mitigate CO_2 emissions into the atmosphere, CO_2 can be exploited as a raw material to synthesize high added-value products (*i.e.* methanol) [1]. The electrochemical reduction of CO_2 is a sustainable and technologically interesting process that, driven by renewable energy sources, can be used to capture and store both renewable energy and CO_2 in the form of chemicals or fuels [2]. However, the main challenge is to find a suitable electrocatalyst to establish this technology at an industrial level. In such context, our group have exploited the basic knowledge of thermochemical catalysis to understand the synergies between these two processes (see Figure 1) and make faster progress in the development of an optimal electrocatalyst [3]. A commercial catalyst (*i.e.* $CuO/ZnO/Al_2O_3$) active for the thermocatalytic CO_2 reduction to CH_3OH at $P = 25$ bar and $T > 200°C$ (with selectivity $\leq 20\%$), was tested for the electrocatalytic CO_2 reduction at atmospheric conditions, demonstrating different products in the C_1-C_3 range with an overall selectivity (faradaic efficiency) of about 70%. Our results paved the way to the development of new and highly efficient electrocatalytic systems for CO_2 capture and utilization by electrochemistry.

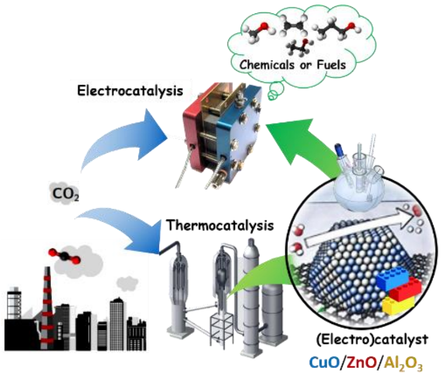

Figure 1. Synergies between thermo- and electro- catalysis for CO_2 conversion to added-value products.

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OR-93

Characterization of conductive molecular wires assembled onto oxide by means of ToF-SIMS

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Nowadays one of the most interesting challenge it is the possibility to integrate the many properties of supramolecular structures on solid substrates. In this communication, we will present the preparation of conductive molecular wires based on polynuclear polypiridinic complex of transition metal. The preparation was carried out by means of an iterative procedure which allowed the controlled assembly of the wires on a oxide surface. First, the inorganic oxide surface was functionalized with zirconil phosphate monolayer and phosphonic group containing a terpyridinic legand was bonded onto it [1]. This platform was exploited for growing the molecular wires based on selected building blocks. In particular, we assembled three different ruthenium containing complexes with iron (II) ions acting as linker between the building blocks. The characterization was realized through ToF-SIMS and UV-Vis spectroscopy in order to diagnose the effective anchoring and monitor the growth of the wires. Thanks to surface sensitivity and high mass resolution of ToF-SIMS, we were able to underline the presence of specific molecular fragment belonging to each one of the three different Ru complexes allowing their discrimination. Finally, we confirmed the growth of conductive molecular wires assembled onto oxide by monitoring the ratio between the molecular signals and the substrate one.

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OR-94

Selective H_2O_2 electrocatalytic generation by cobalt@N-doped graphitic carbon core-shell nanohybrids

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Electrocatalytic oxygen reduction (ORR) is emerging as an interesting synthetic strategy to produce hydrogen peroxide (H_2O_2) in a green and sustainable way [1,2]. N-doped graphitic carbon embedding cobalt nanoparticles prepared from imidazole precursor is proposed as an advanced material able to selectively trigger the ORR to form H_2O_2.

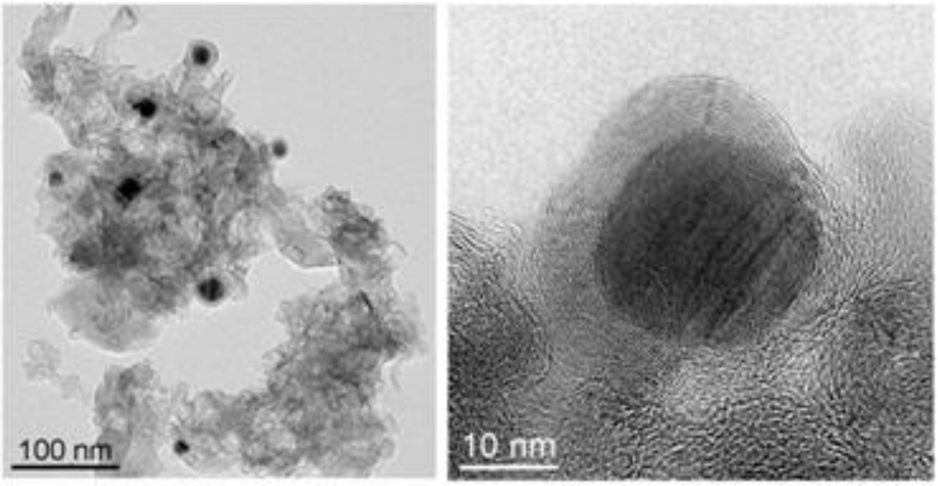

Figure 1. HR-TEM images of N-doped carbon encapsulated Co nanoparticles.

The Faraday Efficiency calculated is almost 100% at very positive applied potentials and the production of H_2O_2 proceeds with high rates (49 mmol g^{-1} h^{-1}) and good current densities (about -0.8 mA cm^{-2} at 0.5 V vs RHE). The dependence of its totally selective behavior has been studied and ascribed to different concomitant features, such as the textural properties, the nature of the metal, the N-type distribution, the acidic environment and the applied potential.

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OR-95

AuPd bimetallic catalysts for lignin-derivatives alcohols valorization

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Lignin moieties consist in three hydroxycinnamyl alcohol derivatives (p-coumaryl, coniferyl and sinapyl alcohols), which differ in the degree of methoxylation on the aromatic ring [1]. Their oxidation to aldehydes is one of the major methods for their valorization. Au-Pd based catalysts effectively oxidize benzyl alcohol (BA), as Wang et al. showed that the Au:Pd ratio on the surface of the particles is a key parameter that influences the catalytic performance [2]. On the basis of these results, here we investigated the effect of the methoxy substituent on catalytic activity of Au-Pd catalysts by studying the oxidation of 4- and 3,4-Dimethoxybenzyl alcohol (4-MBA, 3,4-DMBA) to the corresponding aldehydes. Samples at different Au/Pd ratio were synthesized by sol impregnation.

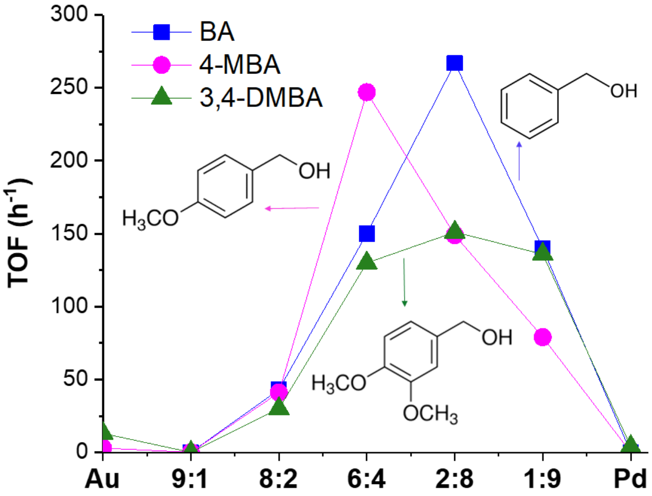

Figure 1. Initial activity. Comparison between Benzyl alcohol (BA), 4-Methoxybenzyl alcohol (4-MBA) and Veratryl alcohol (3,4-DMBA) oxidation.

The presence of the OMe group influenced the catalytic activity, depending on its position. When OMe is in para, we observed a clear difference in catalytic activity by changing the Au-Pd ratio. Contrariwise, a substantial negligible effect of the Au/Pd ratio was detected for 3,4-DMBA oxidation. A deep characterization of the NPs structure will be shown to give some insight on the reaction.

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OR-96

Biochar from pyrolysis of olive waste: natural template for nanostructured polymer filler

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The continuous improvement of the properties is the driving force for material science research.

Use of nanostructured carbon based materials as filler for composites production is a well established practice. Avoiding the expensive high performances materials (*i.e*. CNTs, graphene), biochar can represent a solid alternative. Biochar is the solid residue from pyrolysis of biomass and its structure and properties can be tuned by tailoring the process parameters (temperature, heating rate) [1]. Moreover, it is possible to use the scaffold of the biomass as template to induce a proper microstructure in the biochar.

Taking into account above considerations, we will present and describe a nanostructured carbon material produced through pyrolytic treatment of waste from olive pruning.

The biochar was produced under different pyrolytic regimes and deeply studied using several techniques evaluating the structure and chemical/physical properties. After preliminary characterizations, it was dispersed into an epoxy resin matrix and the mechanical properties of the composites were studied [2].

A tentative relationships between particle size distribution, surface structure and properties of composites will be presented.

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OR-97

A promising enzyme for novel chemoenzymatic synthesis: Linalool dehydratase-isomerase. The catalytic mechanism unveiled by computational investigations

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Linalool dehydratase-isomerase (Ldi) catalyzes reversibly the hydration of β-myrcene to (S)-linalool and geraniol, and the dehydration of geraniol back to β-myrcene. In organic synthesis, harsh conditions are required to perform dehydration of tertiary alcohols in the preparation of olefins, and the presence of other sensitive functional groups limits the scope of substrates. The reverse reaction, i.e. hydration, foresees the nucleophilic attack of a water molecule on a double bond for which acid conditions are usually required and the stereochemical control of the resulting alcohol is challenging. In 2017, Nestl tested the dehydratase and hydratase activity of Ldi on various substrates reporting excellent conformational selectivity and good conversion percentages [1]. The reaction conditions required by Ldi are milder than conventional synthesis and the chemoenzymatic exploitation of this enzyme to obtain olefins or asymmetric alcohols is undoubtedly attractive. Only two crystallographic structures of this enzyme are reported in literature [1,2]. Up to date, the reaction mechanism by which Ldi catalyzes the hydration and dehydration processes is unknown. This work aims to unveil, by Quantum-Mechanical and Quantum-Mechanical/Molecular-Mechanical computations, the catalytic mechanism of Ldi.

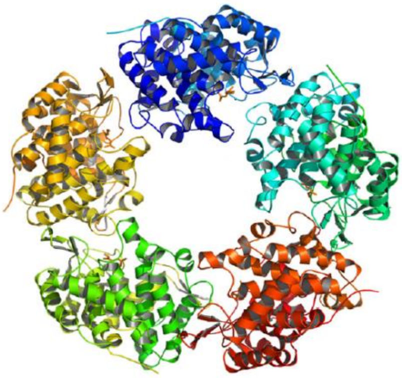

Figure 1. Ldi crystallographic structure.

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OR-98

New synthetic strategies towards organic carbonates and related innovative applications

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Organic carbonates (OCs) are an important class of molecules characterized by a low toxicity and a good biodegradability. Nowadays, cyclic OCs (e.g ethylene carbonate, EC) are synthesized from the corresponding epoxides and CO_2 [1]. On the other hand, the direct condensation of CO_2 and alcohols to yield linear OCs suffers from strictly thermodynamic limitations and needs of high energy input. Therefore, dimethyl carbonate (DMC) is produced by the transesterification of EC and methanol, also referred to as carbonate-interchange reaction (CIR). This reaction is a promising synthetic pathway also for the production of higher OCs. Unfortunately, these are equilibrium-limited reactions, especially for the synthesis of aromatic carbonates. In this context, we have investigated the synthesis of an innovative cyclic aromatic carbonate, the catechol carbonate (CC), starting from catechol and DMC (that act also as the reaction solvent) in the presence of a basic catalyst (either $NaOCH_3$ or ionic liquid). We have developed a reactive distillation system (RDS) able to promote the removal of the co-produced methanol by its selective adsorption inside molecular sieves, an option that finally allowed us to remarkably improve CC yield (ca.95% after 24h) [2]. Afterwards, CC was investigated as an alternative, more efficient carbonate source for the selective synthesis of a wide plethora of both dialkyl and alkylene carbonates in the presence of a basic catalyst. Indeed, the results obtained in very mild reaction conditions (40-80°C, ambient pressure) and low reaction time (30 to 60 minutes) proved an unprecedented outstanding potential of CC, that promoted the quantitative formation of aliphatic symmetric carbonates ($ROCO_2R$) and glycerol carbonate (GlyC) [3]. Finally, a completely innovative and greener synthetic pathway toward 2-hydroxymethyl-1,4-benzodioxane (HMB), a key intermediate for the pharma, has been developed, taking advantage of the peculiar reactivity of GlyC as alkylating agent for catechol (HMB yield up to 88%).

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OR-99

Computational investigation of the effect of external electric fields on organic reactivity

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External Electric Fields (EEFs) can manipulate the reaction path and the chemical output of a reaction. Previous computational studies showed how EEFs may affect the rate and the mechanism of organic reactions [1,2]. The catalytic effect of EEFs in organic synthesis was recently experimentally confirmed by Aragones [3].

In the present computational study, we show how EEFs can affect organic reactivity. As model reactions, we choose the substitution (Mentshutkin reaction) and the electrocyclic (cyclobutenes ring opening) reactions [3].

EEFs modify the energy and the geometry of various critical point along the reaction surface (Figure1). At high EEFs values, we observed a strong catalytic effect along the favoured reaction channel in the absence of EEF or the switch to an alternative reaction channel usually unfavoured.

In particular:

- substitution reactions can undergo a front nucleophilic attack instead of the classic "retro attack";
- 4-electrons electrocyclic reactions, which normally follow outward conrotatory opening pathway, proceed with an inward conrotatory opening pathway and vice versa.

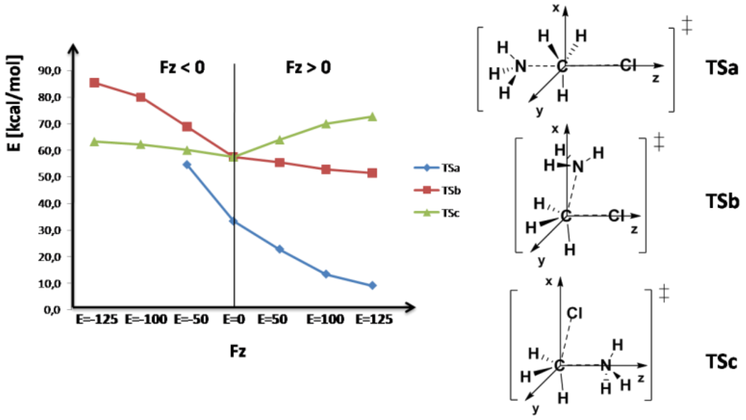

Figure 1. TSs energies, geometry and relative orientation with respect of an EEF along the z-axis for the case of Mentshutkin reaction between methylchloride and ammonia.

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Flash communications

FL-1	Emanuele AZZI	**FL-22**	Maria MARZANO
FL-2	Mariateresa BADOLATO	**FL-23**	Maria G. NIZI
FL-3	Fabio BOLOGNA	**FL-24**	Junwei ZHAO
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FL-21	Marco GIORDANO		

FL-1

Photocatalytic synthesis of tetrahydropyridazines.

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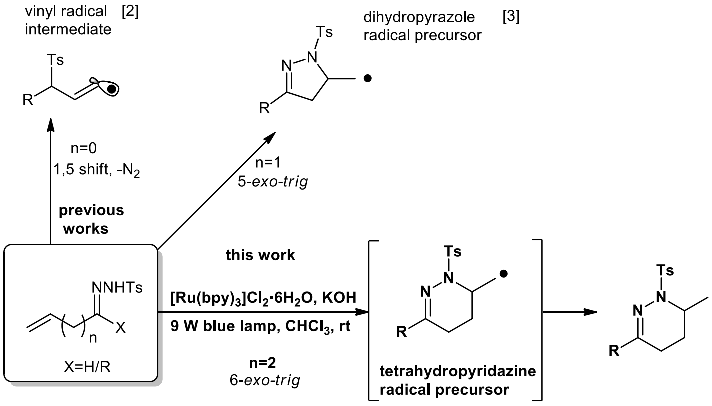
Tetrahydropyridazines are six-membered aza-heterocycles which has proven to be biologically active. Many synthetic routes have been explored for their synthesis, such as condensation of 1,4-keto carboxylic acid with hydrazine, followed by reduction Diels–Alder reactions of 1,2-diaza-1,3-dienes with olefins, and rearrangement reactions [1]. Thanks to the previous experiences of our group with photocatalytic generation of highly reactive radical species from tosylhydrazones, we envisaged the possibility of an alternative visible light-mediated synthesis of these heterocycles.

Our group has described the first example of a visible-light-driven transformation of α,β-unsaturated sulfonylhydrazones leading to a vinyl radical intermediate [2], while a previous work reported how β,γ-unsaturated sulfonylhydrazones undergoes hydroamination reaction to generate a dihydropyrazoles radical precursor [3]. We report how the further shift of the unsaturation to the γ-δ position lead to the formation of a tetrahydropyridazine radical precursor under photocatalytic conditions. Thus, we propose the first example of a photocatalytic synthesis of tetrahydropyridazines, providing these class of molecules exploiting visible light through an eco-sustainable process and mild reaction conditions.



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FL-2

1,4-naphthoquinones: discovery and mechanistic elucidation of a new class of triple-negative breast cancer antiproliferative agents targeting GPR55

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Triple-negative breast cancer (TNBC) represents a clinical challenge with no approved targeted therapies [1]. Recently, correlations have emerged between the expression of G protein-coupled receptor 55 (GPR55) and both TNBC development and invasion, making it a promising key for the development of targeted therapies [2]. The 1,4-naphthoquinone framework exhibits a wide range of biological activities, including anticancer one [3].

A new series of 1,4-naphthoquinones, bearing various cyclic and aliphatic amines on C2, was designed and synthesized to identify antiproliferative agents for TNBC (Figure 1). Among naphthoquinones, compound **2a** and **3a** selectively inhibited the proliferation of MDA-MB-231 cells (EC_{50}=1.6 μM and 2.7 μM, respectively), compared to normal human breast cells MCF10A. Furthermore, they did not affect the viability of peripheral blood mononuclear cells, suggesting their potential safer use for cancer treatment. Molecular docking studies were also carried out to support the *in vitro* results and suggested that compound **3a** could exert its antiproliferative activity acting as a GPR55 antagonist.

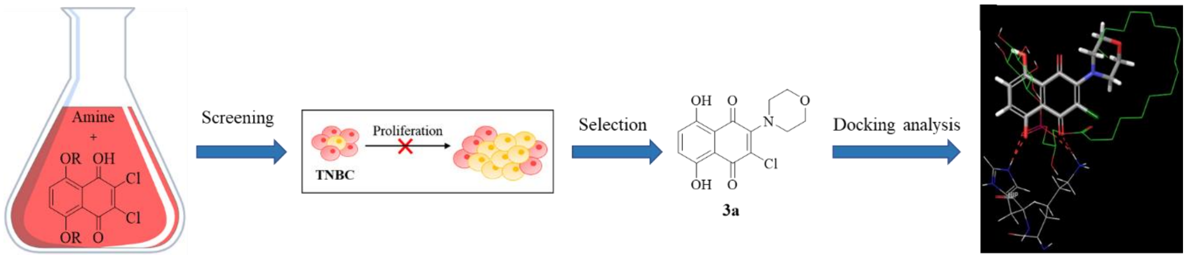

Figure 1. Identification of new antiproliferative agents for TNBC.

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FL-3

High-throughput virtual screening to design protein-gadofullerene hybrids

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Endohedral metallo-fullerenes (EMFs) have great potential as radioisotope carriers for nuclear medicine and as contrast agents for X-ray and magnetic resonance imaging [1].

EMFs have still important restrictions for their use due to low solubility in physiological environments, low biocompatibility, non-specific cellular uptake and a strong dependence of their peculiar properties on physiological parameters such as pH and salt content. Conjugation of the EMFs with proteins can overcome many of these limitations [2,3].

To identify a suitable carrier protein for Gd@C_{82}, we performed docking-based inverse virtual screening on the 1207 protein structures of a large structural database using rigid-body docking programs. The propensity for formation of protein-Gd@C_{82} assemblies was coarsely ranked using the scoring functions of the docking program. The binding energy of the most stable hybrids was computed accurately using the MM/GB(PB)SA method. This protocol led to the identification of potential carrier proteins, or pharmacological targets.

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FL-4

Efficient active-template synthesis of calix[6]arene-based oriented rotaxanes and pseudorotaxanes

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Mechanically interlocked molecules (MIMs) such as rotaxanes, catenanes and related species, are attracting great interest in view of their potential application in materials science, information technology, nanoscience, catalysis and medicine [1]. The growing interest in these species is strictly related to the development of simple and efficient synthetic methodologies that rely on template-directed approaches.

Within this context our research group investigate how the engulfment of a positively charged pyridil-pyridinium-based guest inside the π-rich cavity of a tris-(N-phenylureido)calix[6]arene host affects its reactivity towards a S_N2 reaction [2]. We found that the alkylation of the complexed substrates leads to the formation of oriented pseudorotaxanes and rotaxanes with faster kinetics and higher yields with respect to the standard $S_N2$reaction. More importantly, the strategy described here expands the range of efficient synthetic routes for making mechanically interlocked species with a strict control of the mutual orientation of their nonsymmetric molecular components [3].

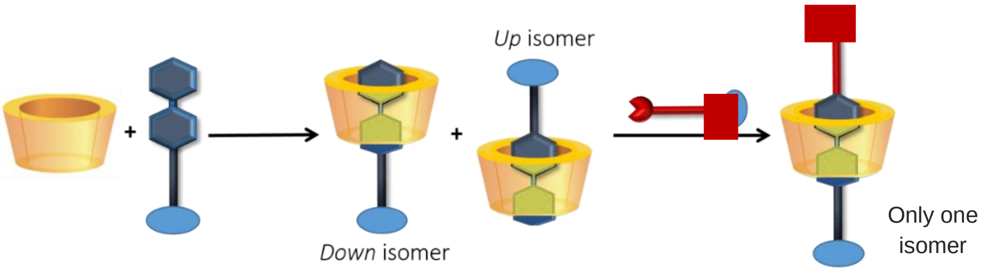

Figure 1. Supramolecularly assisted synthesis of a oriented-rotaxane.

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FL-5

Elucidation of HuR-small ligand binding modes: a combined STD-NMR and *in silico* approach

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Giosuè Costa,[c] M. Yagiz Unver,[d] Daniela Rossi,[b] Anna K. H. Hirsch,[d]
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RNA-protein interactions are essential for the regulation of biological systems as RNA-binding proteins impact every aspect of RNA biogenesis and function. The involvement of these complexes in various pathological pathways has suggested their potential as drug targets unveiling a fascinating route to discover new drugs to modulate gene expression [1]. In this context, the complexes formed by ELAV (Embryonic Lethal Abnormal Vision) proteins and various RNAs have a role in the etiology of cancer, inflammation and neurodegeneration.

Regardless of the recent concept of druggability of ELAV proteins, the development of small molecules able to modulate ELAV-RNA complexes is still at an early stage as both a comprehensive structure-activity relationship and a univocal binding site for small molecules have yet to be determined. Defining the key features required by small molecules to bind ELAV proteins is essential to design new ELAV-RNA complex modulators [2].

Aimed at solving this puzzle, we set up and exploited an STD (Saturation Transfer Difference)-NMR and *in silico* combined approach to study the interaction of ELAV isoform HuR with known complex interferers and structurally related compounds [3].

Regardless of the width of the protein-RNA interface, our approach proved a reliable tool to study HuR-small molecule interactions at the atomic level. Our findings represent a pivotal starting point to drive a drug discovery program, towards a new class of compounds with unprecedented modes of action [3].

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FL-6

A biosimilar mucus model to evaluate the diffusion of drugs for more efficient cystic fibrosis therapies

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Several respiratory diseases such as cystic fibrosis (CF) involve mucus alterations and overproduction [1]. Mucin, that is the principal glycoprotein forming mucus, plays a crucial role for mucus barrier properties which are exposed against pathogens and drugs [2]. Since a strong bind to mucin may reduce the drug pharmaceutical effect, in the first part of this study we investigate the interaction between mucin and some drugs. In the second part of the study, an airway mucus model, which not only imitate the properties of the pathologic CF-mucus but is also suitable for High-throughput screening (HTS) purposes, is developed.

Protein-drug interactions were carried out by UV/Vis and steady-state fluorescence spectroscopy. Alginate/mucin hydrogels were developed by taking advantage of the internal crosslinking mechanism of alginate in presence of Ca^{2+}. Rheological measurements were carried out in order to access the viscoelastic and shear thinning behaviour of the developed gels, and further compared to the pathological CF-mucus.

Association (K_A) and dissociation (K_D) constants at steady state were obtained. The herein mucus model could be further implemented by adding other components of the pathological mucus, therefore giving a much more realistic and complex model.

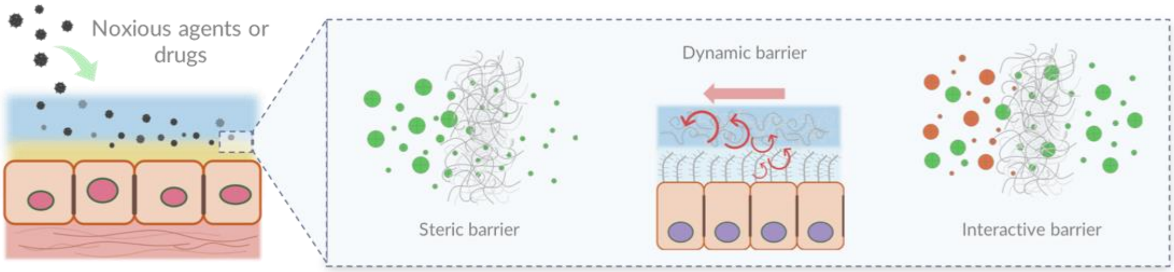

Figure 1. Mucus barrier properties.

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FL-7

Photoactivable 2,5-diaryl tetrazoles as novel scaffolds for assembling selective G-quadruplex ligands

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DNA and RNA sequences rich in guanines are able to assemble into non-canonical secondary structures, known as G-Quadruplexes (G4s), which can be defined as planar macrocycles, held together by hydrogen-bonding interactions. These structures can be found in areas of human genome involved in fundamental processes such as regulation of gene expression, transcription and telomerase dysfunction. Stabilization of G-quadruplex with small molecules able to interact with them is a strategy employed to develop treatments for different kind of pathologies, like cancer and ALS [1].

The synthesis of selective ligands discriminating a G4 among others is a critical point in this research area. In order to produce molecules with high specifity, we decided to apply a novel target guided synthesis (TGS) approach, by using G4 as a template for the reaction [2]. In particular, we chose to exploit "photo-click chemistry", to generate ligands under mild conditions. For our purpose, we decided to employ 2,5-diaryl tetrazoles as photoactivable mojety, previously reported by Lin and co-workers for biorthogonal labelling of proteins [3]. These derivatives, upon irradiation at 310 nm, generate a reactive intermediate, a 1,3-nitrile imine dipole (NI), that can reacts with various dipolarophiles.

We synthesized a library of 2,5-diaryl tetrazoles, functionalized with different types of substituents, in order to evaluate how electronic effect can modulate NI generation and stability.

In our preliminary studies, we investigated spectroscopic properties of photoreactive mojety and, for each compound, we measured quantum yield of NI generation, in aqueous solution. Furthermore, photoreactivity of tetrazoles was fully explored, by irradiation of substrates in presence of different types of alkenes and products obtained have been isolated and characterized.

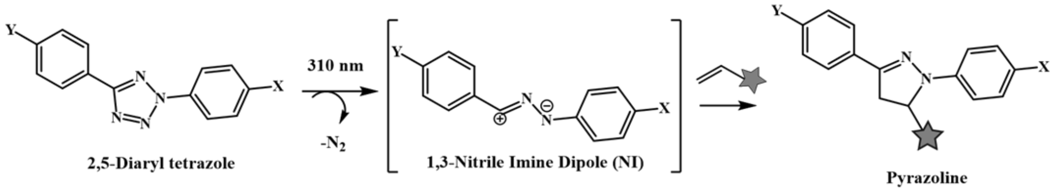

Figure 1. Photogeneration of NI, which can react with an alkene to form a pyrazoline.

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FL-8

Quercetin-3-oleate: bio-catalytic synthesis and efficacy validation in diabetic foot ulcers

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Diabetic foot ulcer is becoming a social problem that affects patients, even at a young age. Several treatments are available but these are invasive and new compounds from natural sources are emerging as new tools for skin repair. From these, the flavonoid quercetin showed good properties although its easy autoxidation limited its therapeutic use [1]. In this context, a lipase-catalyzed esterification with oleic acid was proposed to overcome this limitation [2]. The hybrid quercetin-3-oleate showed good proliferative effects in keratinocyte HaCat cell line and an in intracellular TGFβ expression in skin fibroblast RAT-1 cell line. Docking simulations suggested that the compound could interact with both GPR40 and GPR120 receptors. The hybrid was efficacious in an animal model of skin wounds. In patients affected by diabetic foot ulcer, it favored the wound closure in 3-7 days. In conclusion, the topical administration of quercetin-3-oleate hybrid may represent an effective new pharmacological tool for skin repair.

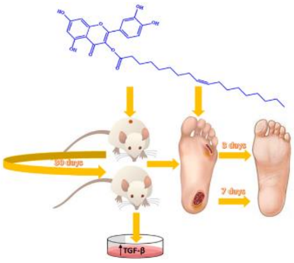

Figure 1. A translational approach applied to quercetin-3-oleate.

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FL-9

Integrating bioaccumulation assessment tools for mammals: from data collection to *in silico* modelling

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The integration of *in-vitro* biotransformation data in a coherent framework for the assessment of mammalian bioaccumulation is one primary objective of the CEFIC LRI ECO44 project "Integrating Bioaccumulation Assessment Tools for Mammals (iBAT-Mam)". Biotransformation is a process that can influence the bioaccumulation of compounds in organisms. Through biotransformation, the parent compound is converted into its metabolites. The potential biotransformation rate of a xenobiotic can be estimated using *in vitro* tests to obtain the in vitro intrinsic clearance (CL_{int}) [1]. Models based on *in vitro-in vivo* extrapolations (IVIVE) and QSAR (Quantitative Structure-Activity Relationships) are used to maximize the information available from *in-vitro* and *in-vivo* measurements.

This work presents preliminary results from the development of a new database of critically evaluated human *in-vitro* biotransformation rates derived from different *in-vitro* assays. Additional data confidence issues such as the presence of duplicated entries, inconsistent structure, multiple data and missing identifiers are presented and discussed.

Finally we develop QSAR models for the prediction of CL_{int} using the S9 *in vitro* assay dataset. The models were developed focusing on statistical robustness and external predictivity. Multiple Linear Regression and the Genetic Algorithm procedure were performed in the software QSARINS by using the theoretical molecular descriptors calculated from molecular structures as independent variables. These results demonstrate that QSAR methods can predict biotransformation rates for humans to improve bioaccumulation assessment.

[1] J.W. Nichols, D.B. Huggett, J.A. Arnot, P.N. Fitzsimmons, C.E. Cowan Ellsberry, *Environ. Toxicol. Chem.* **32** (2013) 1611-1622.

FL-10

Uncatalyzed organozinc halides conjugate addition to enones

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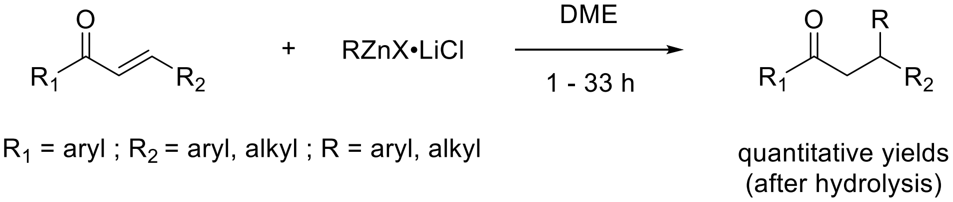
Organozinc halides are interesting reagents from multiple points of view: they are mild organometallics with great functional groups tolerance, they can be obtained by simple and atom-economical methods and, moreover, zinc is cheap and non-toxic [1].

While we were exploring their chemistry to develop a new catalytic method for asymmetric 1,4 addition to enones, we found that, under appropriate reaction conditions, not-enolizable enones undergo uncatalyzed 1,4-addition to cleanly and quantitatively give the addition product (Scheme 1).



Scheme 1. RZnX addition reaction to enones.

The use of dimethoxyethane as solvent seems to be pivotal as well as the presence of LiCl in the organozinc halide formulation.

Although, no optically active products can be obtained, the protocol is of general applicability: as a matter of fact alkyl and aryl zinc halides react cleanly even at room temperature, giving quantitative yields of the addition products and the reaction tolerates the presence of different functional group on the enone substrates.

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[1] A.D. Dilman, V.V. Levin, *Tetrahedron Lett.* **57** (2016) 3986-3992.

FL-11

Development of radiolabeled gold(III) N-heterocyclic carbenes

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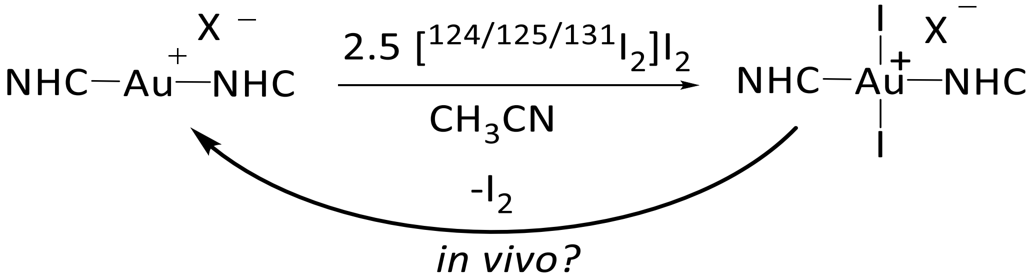
Metal complexes with N-heterocyclic carbenic ligands (NHCs) have found application in both catalysis and medicinal chemistry. Within the field of drug discovery, gold(I) NHCs turned out to be particularly promising because of their relatively straightforward synthesis and their stability in solution. Moreover, biological and targeting properties of this family of compounds can be tuned by modifying substituents on the carbenic ligand. Preclinical studies for gold(I) NHCs showed antiproliferative properties both *in vitro* and *in vivo* and encouraging results on cancer cell selectivity [1]. Despite being less investigated, gold(III) NHCs are also reported to be very active against a range of cancer models *in vitro* and, in some cases, *in vivo* [1,2]. Nevertheless, it is still unclear whether gold(III) NHCs can play a role as active drugs or the observed biological activity is due to reduction with release of the corresponding gold(I) NHCs [1,3].

We synthesized a series of gold (III) NHCs to gain some insights on their role as prodrugs or drugs per se and develop $^{124/125/131}$I-radiolabeling strategies as valuable tools to investigate their *in vivo* biodistribution. This approach could help discriminating between the radioactive gold(III) and the reduced non-radioactive gold(I) species after *in vivo* administration.



[1] M. Porchia, M. Pellei, M. Marinelli, F. Tisato, F. Del Bello, C. Santini, *Eur. J. Med. Chem.* **146** (2018) 709-746.
[2] T. Zou, C.T. Lum, C-N. Lok, J-J. Zhanga, C.M. Che., *Chem. Soc. Rev.* **44** (2015) 8786-8801.
[3] T. Zou, C.T. Lum, S.S-Y. Chui, C.M. Che, *Angew. Chem. Int. Ed.* **52** (2013) 2930-2933.

FL-12

Synthesis of new small-molecule peptidomimetics as selective $\alpha_V\beta_6$ integrin ligands

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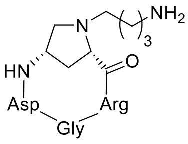
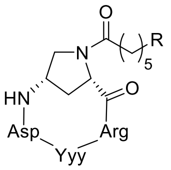
Integrins are heterodimeric cell surface receptors used by cells to communicate with the extracellular matrix; they play key roles in different physiological processes and, for this reason, their altered activity is related to different pathologies including cancer development, metastasis spread, autoimmune diseases and fibrosis, rendering these receptors attractive targets in biomedical research [1]. Among the RGD-recognizing integrins, the $\alpha_V\beta_6$ receptor is overexpressed in many epithelial tumors as well as in liver and pulmonary fibrosis, and has emerged as a biomarker of the epithelial-to-mesenchymal transition, which sustains metastatization, tumorigenesis and fibrosis. Along this line, $\alpha_V\beta_6$ is an ideal target for both therapeutic and diagnostic purposes, provided that potent and selective $\alpha_V\beta_6$ ligands are available.

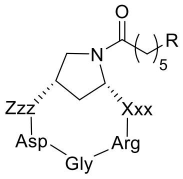


1



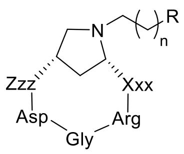
2

Yyy = Gly, Leu
R = N_3, NH_2



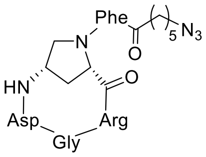
3

Xxx, Zzz = None, Phe, Leu
R = N_3, NH_2



4

Xxx, Zzz = None, Phe, Leu
R = N_3, NH_2
n = 3, 5



5

In this context, our purpose was to synthesize a library of cyclic peptidomimetics where a 4-aminoproline scaffold (Amp) is flanked by variable tri-, tetra- and pentapeptide sequences, and functionalized for the covalent conjugation to bioactive or imaging-active units. Inspired by the known $\alpha_V\beta_3$ integrin ligand **1** [2], we synthesized a collection of 14 cyclopeptidomimetics of type **2-5** by solid phase synthesis, followed by in-solution cyclization reactions. These compounds have been evaluated for their binding affinity toward the isolated $\alpha_V\beta_6$ receptor giving promising results, that will drive us in the development of potent and selective $\alpha_V\beta_6$ ligands as new pharmacologically relevant agents.

[1] S. Raab-Westphal, J.F. Marshall, S.L. Goodman, *Cancers* **9** (2017) 110-138.
[2] A. Sartori, E. Portioli, L. Battistini, L. Calorini, A. Pupi, F. Vacondio, D. Arosio, F. Bianchini and F. Zanardi, *J. Med. Chem.* **60** (2017) 248-262.

FL-13

Enantioselective preparation of the first key intermediate in the synthesis of (+)-oryzalexin S

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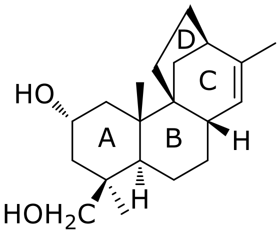
(+)-Oryzalexin S (Figure 1) is a stemarane diterpenoid characterized by the presence of a bicyclo[3.2.1]octane C/D ring system within a tetracyclic skeleton. It was isolated from *Oryza sativa* which produces it when attacked by the fungus *Pyricularia oryzae* or when exposed to heavy metals or when irradiated by ultraviolet light [1,2]. Its structure was elucidated by means of 2-D NMR experiments, but the absolute configuration assignment is still unknown. (+)-Oryzalexin S **1** is the first stemarane type phytoalexin to be reported and it has not yet been synthesized.



1

Figure 1. (+)-oryzalexin S.

Compound **4** is the first chiral key intermediate in the synthesis of (+)-oryzalexin S; in this work we describe the preparation of 4-((1-methyl-2,6-dioxo-cyclohexyl)methyl)-pent-4-enal (+)-**4** and in particular the enantioselective intramolecular aldol reaction of **3**, in the presence of different amino acids and conditions.

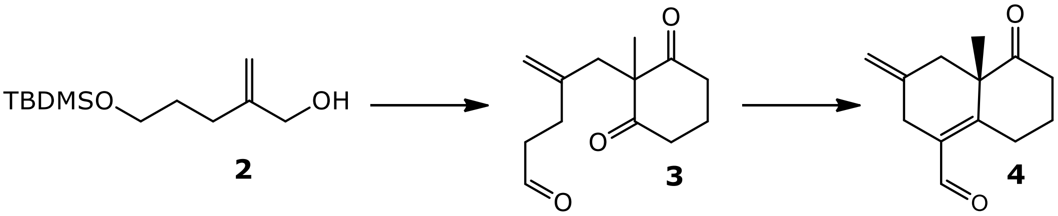


Figure 2. Synthesis of (+)-**4.**

[1] O. Kodama, W.X. Tamogami, T. Akatsuka, *Biosci. Biotechn. Biochem.* **54** (1992) 1002-1003.
[2] S. Tamogami, M. Mitani, O. Kodama, T. Akatsuka, *Tetrahedron*. **49** (1993) 2025-2032.

FL-14

Heterocyclic compounds inhibitors of NS5 RNA-dependent RNA polymerase of Dengue virus

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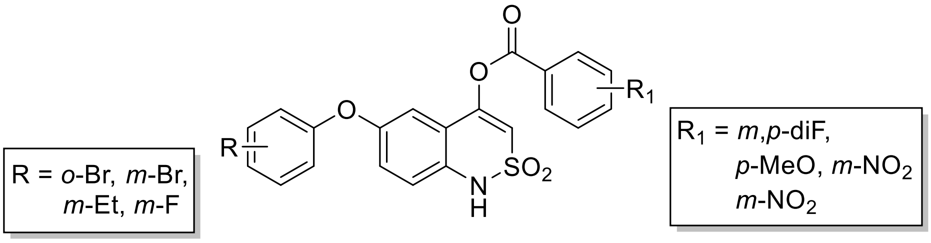
Dengue virus (DENV) is a life-threatening flavivirus that nowadays is undermining the global public health system with estimated 390 million human infections that occur yearly all over the world [1]. To date, no drug is approved for the treatment of DENV infection, thus there is a pressing need for new therapeutics. Among the flaviviral proteins, NS5 RNA-dependent RNA polymerase (RdRp) represents a validated target essential for viral replication and it has no counterpart in humans [2]. Previously, we reported the 2,1-benzothiazine 2,2-dioxides as a new class of non-nucleoside inhibitors (NNI) [3] of DENV RdRp where the C-4 functionalized benzoyl and C-6 phenoxy moieties have a key role in the modulation of the inhibitory potency (Figure 1). In this work, we have designed and synthetized a new series of derivatives where the C-4 and C-6 regions were mainly investigated in order to obtain new SAR information and in some cases, improvements of the physico-chemical properties were observed. Moreover, a scaffold hopping approach was undertaken replacing the previous scaffold with a non-charged core. Finally, the data retrieved from biochemical assays showed that some derivatives resulted equal potent inhibitors of RdRp activity with respect to the initial hit.



R = *o*-Br, *m*-Br, *m*-Et, *m*-F

R_1 = *m*,*p*-diF, *p*-MeO, *m*-NO_2 *m*-NO_2

Figure 1. Representation of 2,1-benzothiazine scaffold and best substituents responsible for NS5 RdRp inhibition.

[1] A.C. Daep, L.J. Muñoz-Jordan, E.A. Eliseo, *J. Neurovirol* **20** (2014) 539-560.

[2] S.P. Lim, C.G. Noble, P.Y. Shi, *Antiviral Res.* **119** (2015) 57-67.

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FL-15

Trichlorosilane: a versatile reagent for nitroalkanes transformations

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Nitroalkanes have proven to be a valuable and versatile class of compounds in organic synthesis. Transformations that permit the interconversion of nitro groups into other functionalities are therefore of primary importance as they potentially broaden the utility of nitroalkanes as intermediates in synthesis [1].

Our group has recently reported an unprecedented metal-free protocol for the reduction of nitro derivatives into amines based on the use of trichlorosilane ($HSiCl_3$) [2], an inexpensive and readily commercially available compound produced as a waste by the silicon industry. Specifically, it was observed that nitro compounds could be reduced to the corresponding amines when reacted in the presence of $HSiCl_3$ and a tertiary amine under mild reaction conditions. However, in case of aliphatic substrates, depending on their nature, the corresponding cyano derivative could be observed as a substantial reaction byproduct.

Herein we report our efforts for the optimization of this protocol that resulted in the chemoselective, divergent transformation of aliphatic nitro compounds into the corresponding amine or cyano derivative by fine tuning of the reaction conditions (Figure 1, unpublished results).

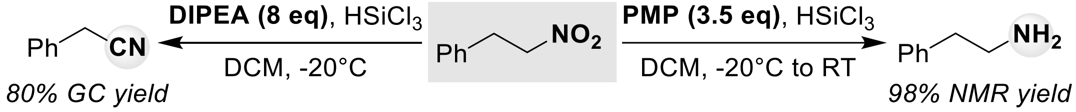

Figure 1. divergent transformation of aliphatic nitro compounds.

The reduction protocol relies on the use of inexpensive and readily available chemicals, features a simple experimental procedure, and is performed under mild conditions. Additionally, the use of transition metals typically used for the reduction of nitro compounds is avoided, providing an environmentally friendly reaction that excludes the contamination of the products by potentially toxic metal impurities.

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[1] M. Orlandi, D. Brenna, R. Harms, S. Jost, M. Benaglia, *Org. Process Res. Dev.* **22** (2018) 430-445.

[2] M. Orlandi, F. Tosi, M. Bonsignore, M. Benaglia, *Org. Lett.* **17** (2015) 3941-3943; M. Orlandi, M. Benaglia, F. Tosi, R. Annunziata, F. Cozzi, *J. Org. Chem.* **81** (2016) 3037-3041.

FL-16

Piperazine thiourea derivatives against clinical strains of colistin-resistant *Acinetobacter baumannii*. Synthesis and *in vitro* biological evaluation

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Acinetobacter baumannii is a typical nosocomial pathogen that is now recognized as a mayor problem in healthcare because its high mortality rate.

In the last years, antimicrobial resistance of different species of *Acinetobacter* has increased substantially and it is resistant to many classes of antibiotics. Colistin is nowadays, one of the last therapeutic options to treat these infections. However, colistin resistant strains are being isolated with higher frequency. Currently, there are no antibiotics commercially available to treat these resistant infections [1].

Based on our previous work [2], we report the synthesis of 4-acyl-1-phenylaminocarbonyl-2-substitued piperazine derivatives, following a short and high yielded methodology, and *in vitro* evaluation of antimicrobial activity against clinical isolated of colistin-resistant *A. baumannii* strains.

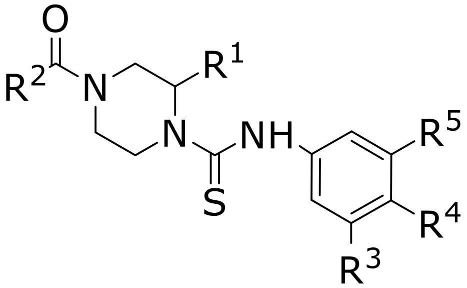

Figure 1. General structure of new compounds.

We have identified four active compounds that showed growth inhibition (MIC 3.12 μM) against 46% of the *A. baumannii* assayed strains and without cytotoxicity. Further studies will need to better identify the specific target for these new molecules and optimize their antibacterial activity.

[1] C.M. Harding, S.W. Hennon, M.F. Feldman, *Nat. Rev. Microbiol.* **16** (2018) 91-102.
[2] J.M. Vega-Pérez, I. Periñán, M. Argandoña, M. Vega-Holm, C. Palo-Nieto, E. Burgos-Morón, M. López-Lázaro, C. Vargas, J.J. Nieto, F. Iglesias-Guerra, *Eur. J. Med. Chem.* **58** (2012) 591-612.

FL-17

Structure-based screening campaign to identify new SAhRMs with immunomodulatory profile

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Aryl hydrocarbon receptor is a ligand activated transcription factor belonging to the basic-helix-loop-helix PAS (PER-ARNT-SIM) superfamily, recently emerged as "druggable target". Nevertheless, receptor promiscuity along with the toxicity of most potent AhR agonists have, so far, limited the development of receptor modulators with immunomodulatory profiles [1].

We have recently characterized the binding mode of two Tryptophan derivatives, namely L-Kynurenine (L-Kyn) [2] and methyl 2-(1H-indole-3-carbonyl)-thiazole-4-carboxylate (ITE) [3], showing how different interaction modalities to the binding site can account for different cellular effects. Considering the growing interest for this target, in this study, we have carried out a structure-based screening campaign taking into account the importance of specific binding modalities of L-Kyn and ITE to AhR and aiming to identify new SAhRMs for the development of novel immunoregulatory agents. Results of the screening campaign enable the identification of novel hit compounds that will be used for analogue-based design for next hit-to-lead optimization studies.

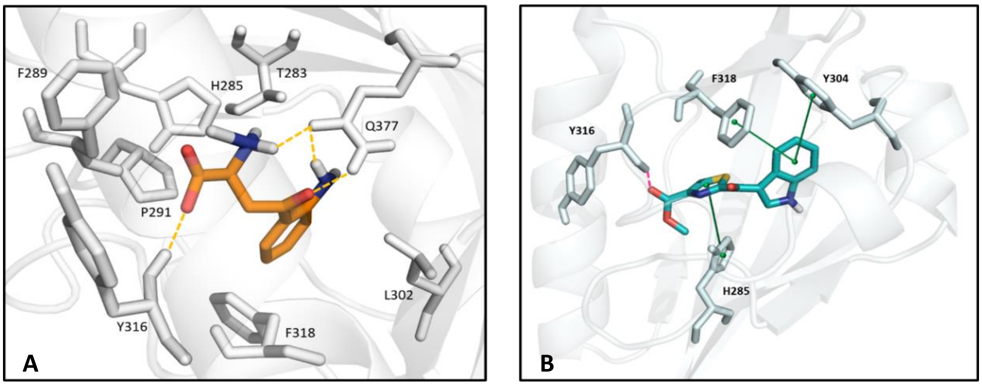

Figure 1. Pattern of interacting residues of L-Kyn (A) and ITE (B).

[1] L. Stejskalova, Z. Dvorak, P. Pavek, *Curr. Drug Metab.* **12** (2011) 198-212.
[2] R. Nuti, M. Gargaro, D. Matino, D. Dolciami, U. Grohmann, F. Fallarino, A. Macchiarulo, *J. Chem. Inf. Model.* **54** (2014) 3373-3383.
[3] D. Dolciami, M. Gargaro, B. Cerra, G. Scalisi, L. Bagnoli, G. Servillo, M.A.D. Fazia, P. Puccetti, F.J. Quintana, F. Fallarino, A. Macchiarulo, *Chem. Med. Chem.* **13** (2018) 270-279.

FL-18

In silico approaches for the refinement of bioaccumulation in mammals

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E-mail: icasartelli@studenti.uninsubria.it

The CEFIC LRI ECO44 project "Integrating Bioaccumulation Assessment Tools for Mammals (iBAT-Mam)" is integrating multiple data streams, experimental and generated by *in silico* approaches, to improve mammalian bioaccumulation (B) assessment. Within this context, models based on *in vitro -in vivo* extrapolations (IVIVE) [1] and Quantitative Structure-Activity Relationships (QSAR) are used to maximize the information available from *in-vitro* and *in-vivo* measurements. For instance, QSARs based on reliable biotransformation rate data [2] and IVIVE estimates can be applied to fill *in-vivo* biotransformation rate data gaps. In addition, quantitative activity-activity relationships (QAARs) can examine interspecies correlations and predict missing information by extrapolating from one species to another.

This study presents the preliminary results generated from the statistical analysis of data for intrinsic hepatic clearance, measured in rodents by different *in-vitro* assays (i.e. S9, hepatocytes, microsomes), which were used to perform IVIVE within the iBAT-Mam project. Descriptive statistics were applied, such as bi- and multi-variate analysis, to evaluate the statistical distribution of experimental responses and to investigate the presence of structural patterns. In addition, preliminary correlation analysis performed between IVIVE clearance data measured in rodents and humans revealed high interspecies correlation >80%. Even though the presence of outliers leaves space for further improvements, the results are relevant for the future development of QSAR and QAAR models within the scope of the ECO 44 Project.

[1] J.W. Nichols, D.B. Huggett, J.A. Arnot, P.N. Fitzsimmons, C.E. Cowan Ellsberry, *Environ. Toxicol. Chem.* **32** (2013) 1611-1622.
[2] E. Papa, A. Sangion, J. Arnot, P. Gramatica, *Food Chem. Toxicol.* **112** (2018) 535-543.

FL-19

Synthesis of benzisoxazoles and their application in the Kemp elimination

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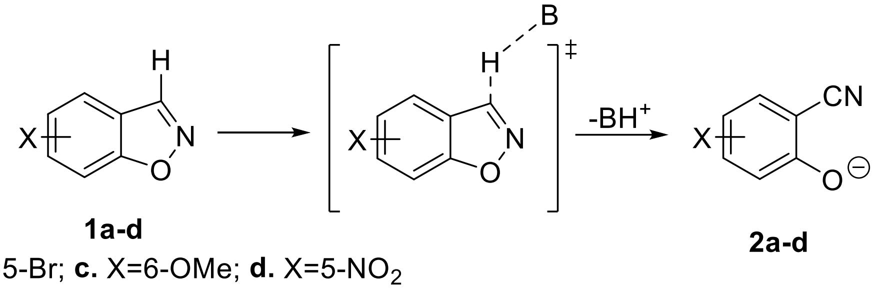
The base-catalyzed decomposition of benzisoxazole to yield 2-cyanophenol is called Kemp elimination (**Scheme 1**), a well-studied benchmark for catalysts design and a model for enzymatic C-H bond abstraction [1,2].



Scheme 1: Kemp elimination.

The benzisoxazoles **1a-d** were obtained through a multistep synthesis in good yields. Formylation of a phenol derivative, nucleophilic addition of hydroxylamine and a final cyclization are the three key steps which afforded the desired fused isoxazole rings.

The base-catalyzed decomposition of synthesized substrates was monitored through UV/Vis spectrophotometry, in order to study the catalytic effect of three hemoproteins, i.e. cytochrome c, myoglobin and hemoglobin. Cytochrome c, myoglobin and hemoglobin catalyze the Kemp elimination after reduction of Fe (III), present in the heme group of all three enzymes, by the ascorbate. Unlike cytochrome c, which catalyzes the Kemp reaction faster than myoglobin and hemoglobin, these latter are deactivated over time: myoglobin is deactivated due to the production of hydrogen peroxide by ascorbate; instead the hemoglobin is deactivated due to interaction with oxygen. The findings from this study suggest that the hemoproteins herein studied catalyze the Kemp reaction through a redox mechanism that implies the presence of Fe (II) in the heme group.

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FL-20

From nature a new compound against *Leishmania infantum*

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Despite the urgent need for efficient medical treatments against Leishmania, today a limited number of drug candidates are available. With the aim to perform a nature-aided drug discovery, we focused on secondary metabolites by *Eremurus persicus* roots. As a result of our investigation, we isolated (*R*)-Aloesaponol III 8-methyl ether, (*R*)-ASME, showing a remarkable antiprotozoal effect against *L. infantum* with an IC50 of 73 µg/mL and not significant toxicity in a macrophage cell line. The potential of this compound have led us to further investigate its properties.

First of all, we optimized the experimental conditions to extract (*R*)-ASME from plant exhaustively. Applying a microwave-assisted extraction (MAE) and using ethanol as solvent, (*R*)-ASME was obtained in high yields (2.5 mg/g dried plant), using low amount of solvent and low waste of time.

In the meanwhile, we have tried to improve (*R*)-ASME solubility. To improve this critical property of the considered *hit*, different molecular modification strategies have been tried. The investigated approaches consisted in the conjugation of (*R*)-ASME with either amino acid, since it is considered a useful method for increase compound water solubility [1], or with an hydrophilic moiety, such as a diethilenglycolic chain. Both of these approaches have brought us to obtain unstable derivates. Further trials will be done considering other hydrophilic groups.

Moreover, to improve cellular uptake, and following a drug targeting approach [2], ongoing efforts will be addressed to prepare a biotin-conjugated (*R*)-ASME derivative. Results will be presented in due course.

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FL-21

Synthesis and characterization of copper complexes as redox mediators in DSSCs

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Over the years, many new redox mediators have been introduced to overcome the limitation of the classical I^-/I_3^- couple in dye-sensitized solar cells (DSSCs). Metal complexes have been identified as potential replacement due to the straightforward tuning of their electrochemical properties in response to structural variations [1]. Co(II)/Co(III) complexes have been reported to be the most performing and providing the best result in DSSC [2]. Nevertheless, these complexes are affected by high metal cost and toxicity which hamper their application on large scale. Copper complexes offer an interesting alternative to overcome the abovementioned limitations, despite a larger visible absorption and a slow the redox processes kinetic.

In this work, three copper complexes-based redox couples have been synthetized and characterized. Sterically hindered ligands allow the preparation of copper complexes with high redox potential but challenging synthesis. We speculate that ligands bearing substituents like methoxy or similar groups in size could be promising redox mediators, combining electrochemical and stability properties, in the preparation of efficient DSSC.

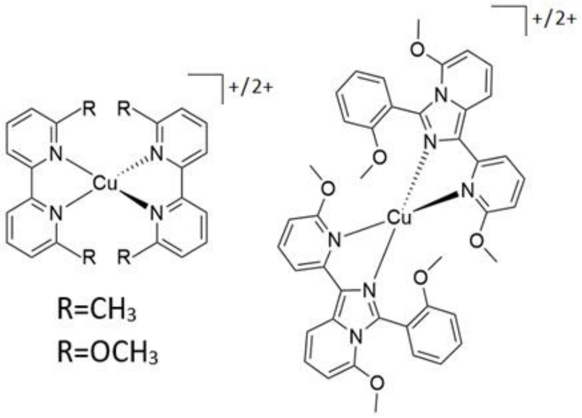

Figure 1: Copper complexes synthesized.

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FL-22

Doubler-end-linked-oligonucleotides: the rules and effects of the linker size on the topology and stability of G-quadruplexes

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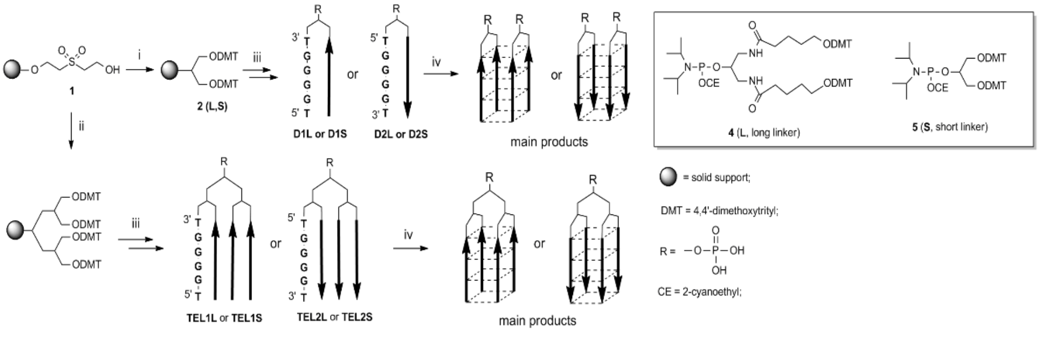
G-Quadruplexes are non-canonical secondary structures of DNA. They are characterized by a core of guanines –known as the G-tetrad– which are stabilized in the presence of cations such as Na^+ and K^+. These structures have drawn attention of researches in medicinal chemistry and more recently in supramolecular chemistry and nanotechnology [1]. However, the formation of the G-Quadruplex scaffold and their structuring in a linear and/or reticulated topology is a difficult process to control. For these reasons, many efforts have been devoted to the design of structural modification that allows multiple junctions. On this ground, in a previous work we have proposed the Tetra-End-Linked-Oligonucleotides (TEL-ODNs), able to fold in G-Quadruplex structures, containing the sequence d(TG4T) well known as model of parallel G-Quadruplex. The results, demonstrated that TEL-$(TG4T)_4$ Quadruplex have a good thermal stability and favorable kinetic and thermodynamic parameters [2]. In this contest we have synthetized the new analogues of TEL-$(TG4T)_4$ containing modification at the linker. These molecules, here named Doubler-End-Linker-ODNs (DEL-ODNs) are characterized by the presence of two G-rich strands attached to a symmetric bifunctional linkers of two different lengths (**D1L,S** and **D2L,S, Scheme 1**) by their 3'- or 5'- ends. The results obtained have allowed a comparison with structures and thermal stability of the tetramolecular $(TG_4T)_4$ and TEL-$(TG_4T)_4$ counterparts (**TEL1L,S** and **TEL2L,S, Scheme 1**).



Scheme 1. Synthetic scheme of TEL-(ODNs) and DEL-(ODNs).

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FL-23

Methoxylated 2-phenylquinoline blocking the *S. aureus* NorA efflux pump

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The rapid insurgence of antimicrobial resistance (AMR) in microorganisms causing difficult-to-treat human infections needs for new strategies aimed to break the resistance [1]. The inhibition of the efflux pumps, overexpressed in many resistant microorganisms and accountable for the extrusion of the antibiotics, represents an innovative route to overcome AMR. Therefore, the challenging approach to identify efflux pump inhibitors (EPIs) is a valid alternative strategy to restore antibiotic activity. The most expressed efflux pump in *Staphylococcus aureus* is NorA, associated with fluoroquinolones resistance.

Previously, we demonstrated that 2-phenylquinoline is a promising scaffold to obtain novel NorA EPIs [2]. Thus, to further improve NorA EPI activity, in this work, we decided to introduce –OMe group/s, already present on known NorA EPIs, in various positions of the unexplored benzene ring of the quinoline scaffold. Seven series of methoxy-quinoline analogues, different on the C-4 *O*-alkylamino chains, selected on the basis of previous results, have been synthesized (Figure 1).

Herein, the design, synthesis and biological evaluation of the new methoxy-2-phenylquinoline derivatives are reported. In particular, some compounds showed excellent results in terms of EPI activity and synergistic effect with ciprofloxacin. Given the interesting overall activity, two of them were selected for in depth studies regarding: *i*) the disruption of the energy required for efflux activity, *ii*) the cytotoxicity evaluation against human cells and *iii*) the metabolic profile [3].

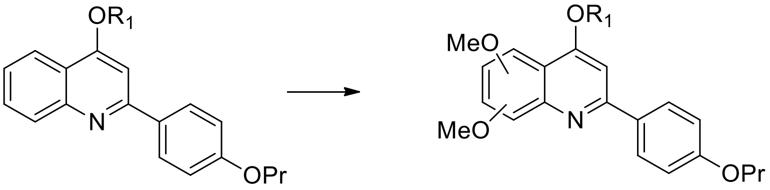

Figure 1. Optimization of the C-4 substituted 2-phenylquinoline core by the introduction of –OMe group/s.

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FL-24

Introducing imidazolidin-2-one scaffolds in peptides promotes the formation of ε-turn

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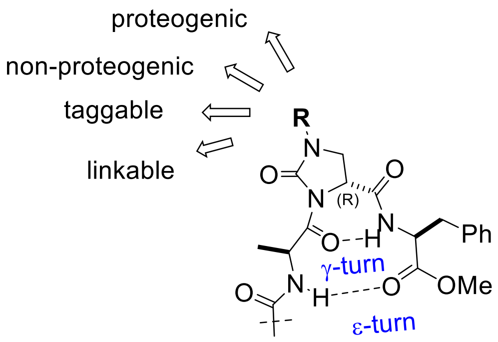
Heterocyclic structures have been widely utilized in pharmaceutical studies to increase metabolic and conformational stability, especially the N-heterocycles. For example, a 5-(aminomethyl)oxazolidine-2,4-dione (Amo) scaffold was introduced in endomorphin-1 to replace proline at position 2 of the sequence, and this made the structure more stable [1]. We have synthesized imidazolidin-2-one-4-carboxylate (Imi) scaffolds within a peptide sequence, and we found that (S)-Imi prefers to form the γ-turn, while (R)-Imi tends to form the ε/γ-turn structure. Compared to the more common and well-studied α-helix, β- and γ-turns, the ε-turn is relatively rare in peptides and proteins. The pseudo-cycle of the ε-turn is formed by a 11-membered H-bond in the opposite direction of the peptide sequence, and usually is accompanied by a classic γ-turn. For the formation of the ε-turn, the distance between C=O···H-N should be ≤ 2.5A, the distance between N···O should be ≤3.2-3.5A, and the N-H···O angle should be 110-120° [2]. According to 2D-ROESY and VT NMR, we found that the trans peptide bond preceding (R)-Imi and the extremely flat structure of the Imi ring, contribute to the formation of the ε-turn. The introduction of proteogenic or non-proteogenic side chains at the position N-1 of the five-membered ring allows introducing the ε-turn in virtually all peptidomimetic sequences. On the other hand, the introduction of functionalized substituents at the position N-1 can be exploited for site-selective reactions, useful for applications such as glycosylation, conjugation with antibodies, fluorescent probes, or for grafting the molecule onto the surface of nanomaterials for drug delivery.



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FL-25

Pyridine-2,6-bis(1H-1,2,3-triazol-4-yl): a selective chelating unit for Minor Actinide extraction from radioactive wastes

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One of the most important scientific and social challenges that humanity faces today is to manage the huge amounts of nuclear wastes accumulated in the last 70 years and to make, possibly, nuclear energy as sustainable as possible [1]. Currently, the PUREX (Plutonium and URanium EXtraction) process is used worldwide to recover Pu and U from the spent fuel while the remainder of the waste contains the minor actinides (MAs) that account for most of the long-term radiotoxicity of radioactive wastes [2]. Interestingly the recovery of these MAs and their separation from Lanthanides would allow to re-use them in novel nuclear fuels thus closing the Nuclear Fuel Cycle. Soft-donor ligands are known to interact more strongly with trivalent actinide ions, An (III), rather than with trivalent lanthanide ions, Ln (III). Recently different heteroaromatic nitrogen donor ligands such as pyridine-bis-triazine ligands were developed showing a remarkable An/Ln selectivity, but most of them suffer of kinetic or stability problems in the harsh extraction condition [3]. In the last few years we have been exploring different chelating units based on heteroaromatic nitrogen ligands and found that the "clicked" pyridine-bis-triazole unit is rather effective and selective in An/Ln extraction. We herein report the synthesis of both hydrophilic and lipophilic ligands based on pyridine-bis-triazole unit, showing their ability to effectively and selectively separate An from Ln even at very high nitric acid concentration and in the presence of other fission products.

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FL-26

Synthesis of phosphonodisaccharide analogue from *Neisseria meningitidis A* capsular polysaccharide

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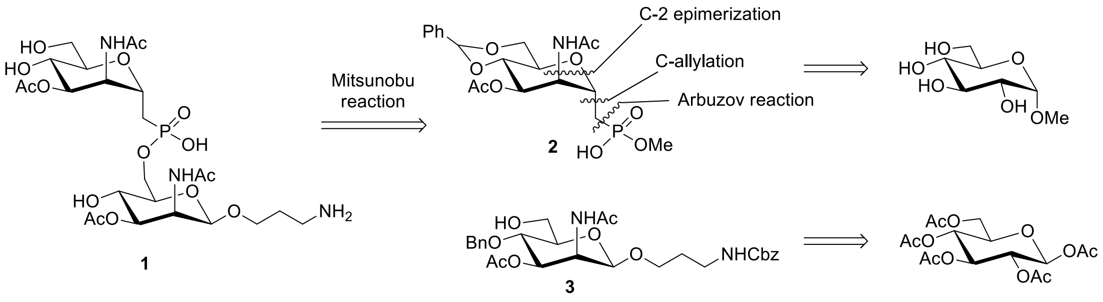
Neisseria meningitidis, a Gram-negative bacterium, is one of the major causes of bacterial meningitis. Serotype A (MenA) is the main responsible for epidemics in sub-Saharan Africa. The structure of MenA capsular polysaccharide consists of (1→6)-linked-2-acetamido-2-deoxy-α-D-mannopyranosyl phosphate residues acetylated at C-3 to an extent of 70-90%. The natural polysaccharide, once isolated, results to be not stable in aqueous formulations due to the intrinsic lability of the anomeric phosphodiester linkages. Isosteric phosphono analogues, previously synthesized by our group, proved to be much more stable to hydrolysis and to be recognised by anti-MenA serum [1]. Since recent studies revealed that 3-*O*-acetylation is crucial for immunogenicity [2], we decided to synthesize the 3-*O*-acetylated phosphono analogue, focusing our attention on the disaccharide **1** (Scheme 1) due to its intriguing immunogenic properties.

The target molecule **1** could be achieved by Mitsunobu coupling of phosphonate **2** with mannoside **3** which bears an amino spacer suitable for conjugation. Acetyl group could be installed at C-3 early in the synthesis. The correct sequence of key transformations (Scheme 1) must be carefully considered to obtain phosphonate **2**. In this communication we describe the strategies we explored for an efficient approach to methylphosphonate **2** as key precursor of target compound **1**.



Scheme 1. Retrosynthetic strategy.

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FL-27

Catalytic assessment of zeolite-based systems for dimethyl ether synthesis

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Dimethyl ether (DME) is recognized as an eco-friendly alternative fuel for Diesel engines as well as an intermediate for production of both olefins and gasoline-cut hydrocarbons. DME can be produced via either dehydration of methanol or one-pot CO/CO_2 hydrogenation by using acids or metal/acid multifunctional materials as catalysts, respectively [1].

Whatever the process, the features of acid function strongly affect DME yield and catalyst deactivation, consequently affecting process costs. In the last years, the utilization of zeolites as acid catalysts has received a renewed attention due to important advances in zeolites field [2]. In this work, the effect of features of home-made zeolites on catalytic behavior during DME synthesis via both methanol dehydration or CO_2 hydrogenation is discussed at the light of recent works. High DME yield were achieved on zeolites in comparison with commercial γ-Al_2O_3 catalyst but both catalyst stability and coke formation strongly depend on zeolite properties, such as channel system, acidity and crystal size. In this concern, among the investigated zeolites (e.g. MFI, FER, BEA, MOR, EU-1, etc.), high-alumina FER-type zeolite nanocrystals exhibit the best performances in terms of DME yield, deactivation and coke formation.

Although several investigations have been carried out in this field, more challenges are still opened for further investigations towards reaction mechanism and catalyst stability during CO_2-to-DME process [3].

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FL-28

Ambient condition fabrication of perovskite solar cells

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The power conversion efficiency of perovskite solar cells (PSCs) has remarkably increased, in just a few years, from 3.8 to 22.7%, due to the excellent properties of organometal-halide perovskite, such as strong and broad optical absorption form visible to near infrared, high electron and hole diffusion length and a low surface recombination velocity [1]. Nevertheless, PSCs are susceptible to oxygen and water, because of a degradation pathway leading to the formation of lead iodide, methylammonium and hydrogen iodide. For this reason, perovskite materials require high temperature and glove-box synthetic conditions, thus hindering large-scale applications.

During last year, a few efforts have been made in the development of ambient condition fabrication strategies, such as thermal engineering [2] and the use of anti-solvents [3]. In the first case, the substrate TiO_2 is pre-heated at low temperature before spin-coating deposition of perovskite precursors. This ensures phase purity and a pinhole-free morphology, with a PCE reaching 12%. In the second case, the use of anti-solvents reduces the solubility of perovskite precursors, thereby promoting fast nucleation and rapid crystallization. In this way, the effect of air-moisture is less relevant.

In conclusion, the fabrication of PSCs in open air atmospheric conditions is challenging, but necessary for photovoltaic application of perovskite materials.

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FL-29

Metadynamics as a tool for studying the reduction mechanism of Asplatin, a Pt(IV) prodrug

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Pt(IV) complexes are an emerging novel class of anticancer drugs. They can act as pro-drugs, which are activated inside the cells by reducing agents such as L-glutathione or L-ascorbic acid and can release by various mechanisms the active square-planar Pt(II) species and the ligands in axial position. In addition to their increased kinetic stability, the further advantage of the use of Pt(IV) prodrugs is the possibility to choose the axial ligands properly tuning their pharmacokinetic properties.

Aiming at contributing to the elucidation of the mechanism of the key reduction step of Pt(IV) prodrugs, the activation by reduction of the recently synthesized Asplatin Pt(IV) complex, *c,c,t*-$[PtCl_2(NH_3)_2(OH)(aspirin)]$ [1], in presence of L-ascorbic acid as reducing agent was investigated. After a thorough static quantum-mechanical DFT study [2], the metadynamics sampling technique, which allows to explore the different paths of reduction and tracing the relative surface of free energy, was applied to investigate the reduction process of the complex.

Here we highlight the importance of the application of this technique in the future study of the unknown working mechanisms of new and old complexes.

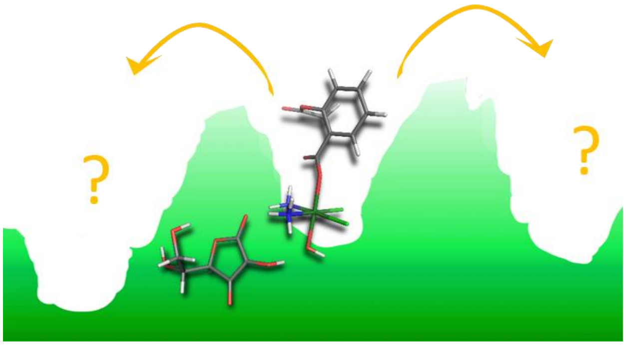

Figure 1. Metadynamics study of Asplatin.

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FL-30

Sequestration of lanthanide ions from aqueous solutions with synthetic saponite slays

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Due to their unique electronic, magnetic, optical and catalytic properties, the rare-earth elements (REEs) have been extensively used in the last decades in renewable energy and for state-of-the-art energy-efficient technologies (*i.e.* batteries, solar panels and high-performance magnets). Thus, the recycling of REEs is of great importance to reduce costs related to the use of such elements. Furthermore, there is also an environmental problem related to the release of lanthanide ions associated to nuclear accidents, resulting from the fission of uranium and plutonium isotopes, and from other sources. Actually, the traditional processes employed in lanthanides recovery are based on solvent extraction, which require several steps and involve large amounts of solvents. The development of environmental remediation/recovery methods with higher efficiency, lower costs and environmental impact is an important challenge for the scientific community. In this respect, several solid sorbents based on carbon, porous silica and layered materials have been selected for their high chemical affinity for *f*-block species.

In this work, we explored the possibility to use two synthetic saponite clays (SAP) with different lamellae dimensions as solids sorbents for the extraction of lanthanides ions with different ionic radius (La^{3+}, Gd^{3+} and Lu^{3+}) from aqueous solutions. The saponites were characterized by different particle size and cation exchange capacity (CEC). The uptake studies of Gd^{3+} were performed in pure water and in simulated seawater solutions, in wide concentration ranges of Gd^{3+} (10-0.1 mM). Both the saponite solids showed good effective sorption capacity. A relationship between the uptake capability of Gd^{3+} and the CEC of the clays was observed. The uptake of Gd^{3+} is comparable to that of other layered and microporous materials reported in literature. The same behavior was found for the extraction of La^{3+} and Lu^{3+} ions. The solids were also tested in the presence of an equimolar mixture of La^{3+}, Gd^{3+} and Lu^{3+} ions: in this case, a strong selectivity for the ion with lower ionic radius (Lu^{3+}) was observed respect to the other two lanthanides.

FL-31

Creating hierarchical sapo-34 architectures with tunable acid properties using bottom-up synthetic strategies

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Hierarchical zeolites or zeotype materials, which combine micro and mesopores in a multilevel pore network, strongly emerged as novel materials for catalytic applications to overcome typical drawbacks of traditional microporous materials such as poor mass transfer and hindered diffusion. In spite of the progress in novel synthetic strategies to produce hierarchical materials, significant challenges are still ahead. In fact, the contribution and the properties (connectivity, surface area, pore size and distribution, pore volume etc.) of the secondary porosity strongly depend on the method used for its development.

In this contribution, two novel bottom-up routes were used to synthesize hierarchical SAPO-34 catalysts, mitigating the need of sophisticated surfactants or templates by using: (i) CTAB encapsulated within ordered mesoporous silica (MCM-41) as both the silicon source and mesoporogen [1]; (ii) a di-saccharide as structure directing agent to direct the mesopore network [2]. To assess the nature, strength and the accessibility of the acid sites in the hierarchical zeotype catalysts, a fine physical-chemical characterization using FTIR spectroscopy of adsorbed probe molecules together with solid state NMR was performed. In addition, structural and textural properties of the hierarchical zeolites were also explored by means of XRD and volumetric analyses.

The hierarchical SAPO-34 catalysts showed superior activity in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam (precursor for Nylon-6) with respect to the parent microporous systems, thanks to the overcoming of the diffusion constraints due to the introduction of mesoporosity.

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FL-32

Identification of artistic pigments: a comparison of different approaches to image acquisition and analytical data processing

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In the manipulation of Cultural Heritage artworks for identification or attribution or in view of conservation and restoration purposes, the availability of non-destructive, portable, straightforward, rapid and efficient analytical systems represents a key issue in chemical diagnosis. Anyway, as far as pigments or dyes are concerned, a main difficulty is represented by the fact that color is an "exhibition" of matter not easily measurable, and hence not easily communicable, because it is the result of a subjective response to a photostimulation of visual receptors.

The project outlined herein keeps account of such aspects of the analytical determination of color, with the aim of evaluating the possibility that a reproducible, objective definition of chromatism could be achieved by means of a proper processing of analytical data [1,2] obtained with a fast, easy, portable, relatively cheap and absolutely non-invasive acquisition technique such as photography, colorimetry being used for comparison sake.

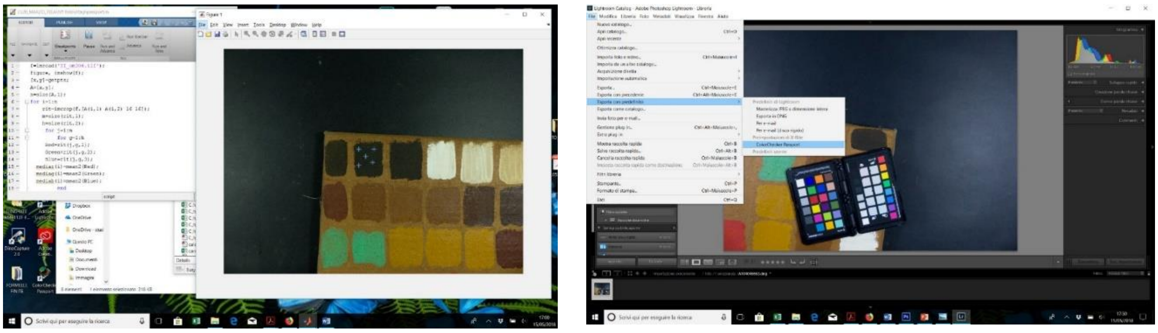

Figure 1. Methods for color calibration: application of MATLAB (left) and of X-RITE plugin (right).

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FL-33

Ionic liquids based electrolytes for advanced cathode materials

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Development of new materials for Li-ion batteries is mandatory to satisfy the increasing demand for systems delivering higher capacity, energy density, cycle life stability and safety [1]. Looking at the cathode side, substantial efforts have been done on the design and optimization of emerging positive electrode materials displaying large capacity values (>200 mAh/g) and/or high average voltages (>4 V vs. Li/Li^+) [2]. Promising candidates are the transition metal phopsho olivines and the mixed metals layered oxides. However, to take advantage of the above mentioned properties it's very important the availability of a electrolyte stable at high operating voltages. In fact, such cathode materials have their operating voltage above the anodic cut-off voltage (4.3V) of the most used carbonate-based electrolytes. This means that side reactions can occur during charge at voltage higher than 4.3V including the formation of thick solid electrolyte interface layer on the electrode surface, high initial irreversible capacity loss and production of gaseous reaction product [2]. On the contrary, the use of an ionic liquid possessing a wide electrochemical window as solvent in the electrolyte solution proved to improve the electrochemical stability of these materials and consequently they can be safely used as cathode in a Li-ion battery [3].

Here, the influence of the addition of $[Pyr_{1,4}]TFSI$ and $[Pyr_{1,5}]TFSI$ on the electrochemical properties of two carbonate-based electrolytes, i.e. 1M $LiPF_6$ in EC:DMC=1:1 v/v and 1M LiTFSI in EC:DMC=1:1 v/v is reported. The new electrolyte composition have been prepared and characterized.

We investigate the electrolyte stability window by linear sweep voltammetry and cyclic voltammetry to see the electrochemical stability of electrolytes. Potentiostatic-polarization measurements are used to calculate lithium transference number and lithium stripping deposition are made to show the overpotential during cicling. Once analyzed several electrolyte mixtures with ionic liquids, we evaluate their effect when used in a lithium cell with Lithium Iron Phosphate as cathode.

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FL-34

Double-cable copolymers for polymeric solar cells

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Polymeric solar cells (PSCs) have been widely studied in the last few decades since this technology offers many potential advantages over the most employed silicon-based ones, such as light weight, flexibility and easy tuning of the optoelectronic properties.

Currently, the most successful and employed architecture for the fabrication of high-performance polymeric photovoltaic solar cells is a bi-continuous network of an electron-donor (a conjugated polymer) and an electron-acceptor (fullerene or its derivatives) material, called bulk heterojunction (BHJ). On these bases, to achieve optimal phase segregation between the donor and acceptor molecules for the charge generation, the synthesis of donor-acceptor double-cable polymers appears particularly interesting [1].

Starting from soluble, regioregular (PT6BrR) and regiorandom (PT6Br) homopolymeric precursors, new alkylthiophenic copolymers bearing the bromine atom and C_{60}-fullerene group at the end of a hexylic side chain inserted at position 3 of thiophene have been prepared. The structural and photophysical properties of the above derivatives were investigated by gel permeation chromatography (GPC), ^{1}H-NMR, thermal analysis (DSC, TGA), UV-Vis and FT-IR spectroscopy. Homo- and copolymers were also tested as photoactive layers in organic solar devices, respectively blended with $PC_{61}BM$ (1:1 w/w) as the acceptor material and as double-cable materials.

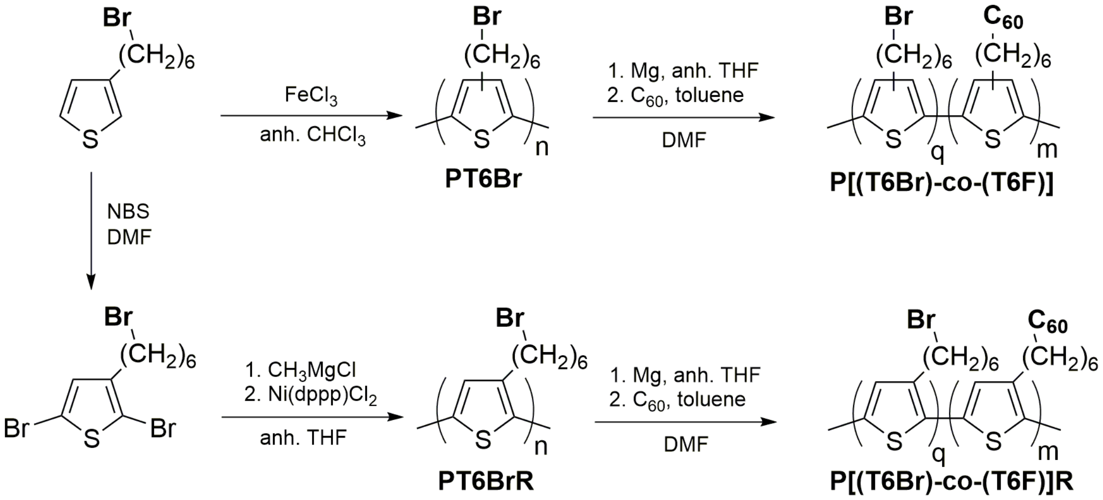

Figure 1: Synthesis of homopolymers and copolymers.

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FL-35

Investigation on paint thinners quality: development of analytical methods for determination of composition and metal content

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Paint thinners are a class of products that are involved in many industrial processes. It’s a known fact that, sometimes, those products could be reused, after a regeneration process, to lower the cost of production in some stages, instead of using virgin paint thinners. In this case it’s important to being able to distinguish between virgin and regenerated solvents to avoid commercial frauds that could occur if those products are sold as brand new if they are not. Two indexes of low quality of those solvents are metal traces content and their own composition in terms of organic compounds. The aim of this work was to develop analytical methods to evaluate those parameters. In both determinations, of metals and organic compounds, were compared certified virgin, regenerated and exhausted paint thinners to commercial products in order to evaluate their quality. For what concerns metal content (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn were investigated). It was initially explored a wet digestion method, using at first nitric acid on the dry residue and then sulfuric and perchloric acids to complete mineralization. Samples treated that way were then analyzed in ICP-OES. For comparison the same samples were treated by incineration and ash digestion using aqua regia. Even Hg and As were analyzed using, this time, HGAAS. Wet digestion method showed worse reproducibility than incineration, but better results for volatile metals such as Pb, Cd and As. In order to determinate organic composition of the paint thinners dry residue was analysed using IR spectrometry and main composition was determined using GC-MS in 3 slightly different method to find all volatile and semi-volatile compounds. In this case, variating initial column temperature and injection technique was possible to separate high molecular mass and low molecular mass compounds. Those method were used as complementary, because of their weak spots and strong sides. Qualitative and semi-quantitative analysis were performed. Results showed that commercial products we exanimated are not usually comparable to virgin paint thinners, but are near to regenerated ones for what concerns metal content and, mostly, their organic composition. In many cases the label declared content did not match with the real composition of those products, index of bad quality and possible regeneration, leading to a commercial fraud.

FL-36

Sensing features of silver nanoparticles green generated and reshaped

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In advanced sensing applications, plasmon resonances induced by metal nanoparticles (NPs) serve as sensitive probes to detect local variations in the surrounding environment at the molecular level. Another advanced application it’s the surface-enhanced Raman scattering effect that occurs when NPs are used as substrate. Thanks to this effect it’s possible to detect analytes, like protein at even picomolar concentration[1]. The sensing features of NPs depends on the dimension, shape, and purity of their surface[2]. For this reason, we synthesize Ag NPs by Laser ablation in liquid using no chemicals except for trisodium citrate. Moreover, we reshape the produced nanoparticle with a new, chemicals free method by Laser reirradiation in liquid[3]. Then we studied the Raman enhancement factor and the dipole sensitivity of the synthesized NPs.

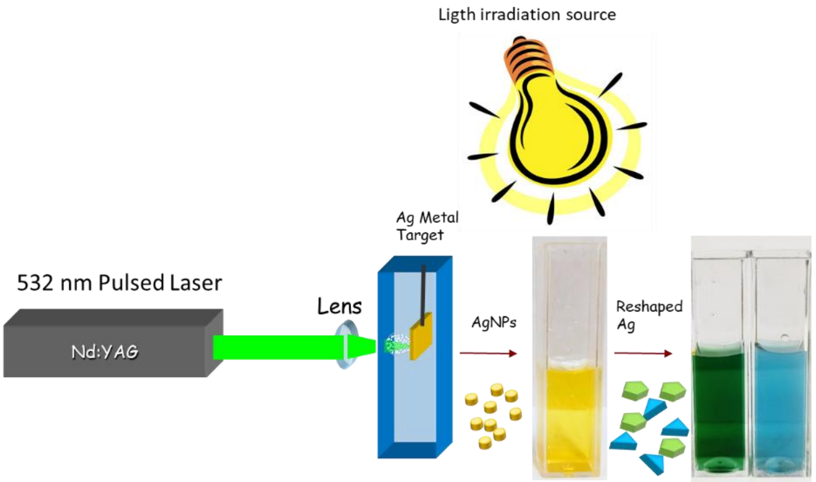

Figure 1. Experimental setup for synthesis and reshaping process of Ag NPs.

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FL-37

By-products analysis of a pyrolysis plant powered by plastic waste materials for energy's production

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Alternative and renewable energy supply sources are going to play an increasingly strategic role in the global landscape. Among them, the waste plastic materials produced by our society are remarkable, establishing a potential renewable source. However, it is known that waste-recovery and recycling technologies are very often expensive. When these technologies aren't workable or not economically convenient, taking an advantage of them by recovering the energy in the so-called "quaternary recycling", using the plastic materials as alternative fuel, could be very useful [1]. For example, waste plastic materials are usually transferred to landfills or to incinerator, but it cannot be ignored that during the combustion process there is a high risk of oxygenated heterocyclic compounds development (e.g. dioxins) as well as polluting substances generation from combustion itself (e.g. polycyclic aromatic hydrocarbons PAHs). In collaboration with private company equipped with an experimental pyrolysis plant fed by waste plastic materials coming from automotive industry, it was possible to characterize its byproducts.

Synthetically, the process allows these plastic materials to be transformed into combustible gas through a slow pyrolysis at temperatures between 400 to 650 °C, thanks to a heating induction's system. This work was focused on the analysis of organic compounds (such as PAHs and polychlorinated biphenyls PCBs) and the determination of some anions on carbon black, ashes, bitumen and washing waters. GC-MS analysis showed a quite high amount of PAHs in all the samples, above all in the bitumen. PAHs detected was those with low molecular weight, then with a low toxic equivalency factor. Instead, GC-MS analysis didn't detected any PCBs in all samples. In addition amount of anions were under the law limits.

In conclusion, to verify the versatility of the pyrolysis process in its industrial application, the analytical characterization of the above-mentioned parameters is particularly important, also in view of future legislative measures on the environment on the potential residual plastics as a renewable energy resource.

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FL-38

Hydrophobization of nanomaterials for application in leather finishing

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Leather are mainly composed of proteins containing amino-, hydroxyl, carboxyl groups, naturally causing its hydrophilicity. Consequently, leather products are exposed to a damage by water and bacteria [1]. Nowadays, the techniques applied to fulfill this requirement employ non-sustainable products containing perfluoroalkylated substances (PFAs).

On the other hand, properly functionalized ceramic nanomaterials represent an alternative innovation to pass to "greener" processes and materials.

In this respect, the research is focused on the preparation and characterization of nanoparticles functionalized with highly branched alkyl chains to obtain hydrophobic surfaces. The next step of this study is the application of the modified nanoparticles in sprays for leather coating.

The starting point is to reproduce existing protocols that show the potential of nanomaterials for preparation of hydrophobic coatings [2], and its application to silica nanoparticles to obtain more stable covalent bonding of hydrophobic agents to the nanoparticles surface.

Since silica nanoparticles are already used in leather finishing process, they may play an additional role upon functionalization.

From IR and NMR measurements it is possible to observe the amide bond formation between hydrophobic agent and silica surface. Moreover, microgravimetric measurements allowed to evaluate the effectivness of the functionalization, due to the decrease of the material adsorption capacity towards water.

This is the basis for further application of silica nanomaterials in leather treatment and for following study of their interaction with the main component of leather, the collagen.

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FL-39

Serum bile acid quantification in anti-TNF alpha treatment for intestinal bowel disease combined to multivariate chemometric data analysis

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Bile acids (BAs) are endogenous steroids and they play an active role in several physiological functions. They are involved in transport of lipids in the enterohepatic circulation, but BAs have also been recognized as molecular signaling hormones [1]. Primary BAs synthetized in the liver undergo several metabolic pathways in liver and intestine by gut microbiota. There is an important rationale in the study of BA composition where a deficient intestinal absorption might account for a distorted BA homeostasis as in intestinal bowel disease (IBD). Indeed, a compromised gut microbiota could modify the overall BA quali-quantitative composition in plasma, bile and intestine [2]. Consequently, BA plasma levels may reflect IBD conditions, like in Crohn disease (CD) and ulcerative colitis (UC). The BA pool alteration must be carefully studied and only a complete characterization of BA qualitative composition, rather than total BAs, can be correlated to disease clinical biomarkers.

The present study aim was the profile determination of serum BAs in IBD patients treated with an innovative anti-TNF alpha biological therapy in comparison to conventional theraphy and healthy subjects. A sensitive and selective HPLC-ESI-MS/MS method was fully validated for the analysis of BAs in human plasma. Up to 15 different BAs, including free and glycine/taurine conjugates, alongside patient biochemical and medical parameters where admitted to a principal component analysis (PCA) to assess whether is possible to discriminate IBD disease from healthy conditions and verify the therapy efficacy. Results proved a good discrimination between CD and healthy patients basing on glycine conjugated-BA variations, while for UC such model was not valid.

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FL-40

Synthesis and characterization of a novel azo dye-based cerium(III) metal organic framework

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Metal Organic Frameworks (MOFs) have attracted a lot of interest in the last decades because of their potential application in the storage, separation and conversion of gases, (photo-)catalysis, drug delivery, optoelectronics, sensors, ferroelectricity, light harvesting and energy transfer [1]. Different organic linkers have been used in the synthesis of MOFs with particular attention to those conferring photo-responsive properties.

We have focused our attention to azo-based dyes due to their straightforward synthesis, good photostability and robustness in MOF preparation pathways. Here we introduce the synthesis of a new azo dye-based Cerium MOF [2] starting from the azobenzene-4,4'-dicarboxylic acid and Ce(III) nitrate whose synthesis procedure was optimized by high-throughput methodologies [3]. The new material was characterized by single crystal and powder XRD, TGA, optical spectroscopy, N_2 and CO_2 adsorption volumetry and quantum-mechanical calculations.

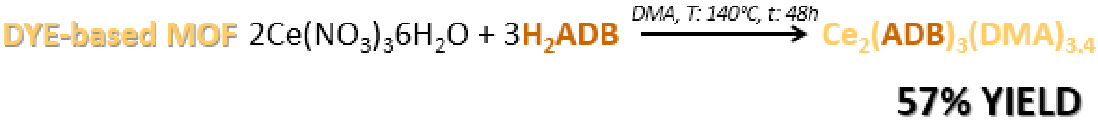

Figure 1. Synthesis of $Ce_2(ADBC)_3$*3,4DMA optimized by means of high throughput methods [3] under solvothermal conditions.

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FL-41

Spectroelectrochemical characterization of kuquinones anions

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KuQuinones (KuQ) are highly aromatic pentacyclic quinoid compounds synthesized in our lab [1]. These molecules show interesting electronic and electrochemical properties such as a broad absorption spectrum in the visible region and three reduction processes. In particular the first one has a favorable reduction potential with respect to simpler quinoid compounds. Due to these characteristics two appropriate KuQ's derivatives were used as photosensitizer in photoelectrochemical devices obtaining good results in terms of efficiency [2,3]. In order to fully characterize active reduced species of KuQs we are currently investigating their nature through spectroelectrochemical measurements.

In this contribution, preliminary characterization of KuQuinones anions will be presented.

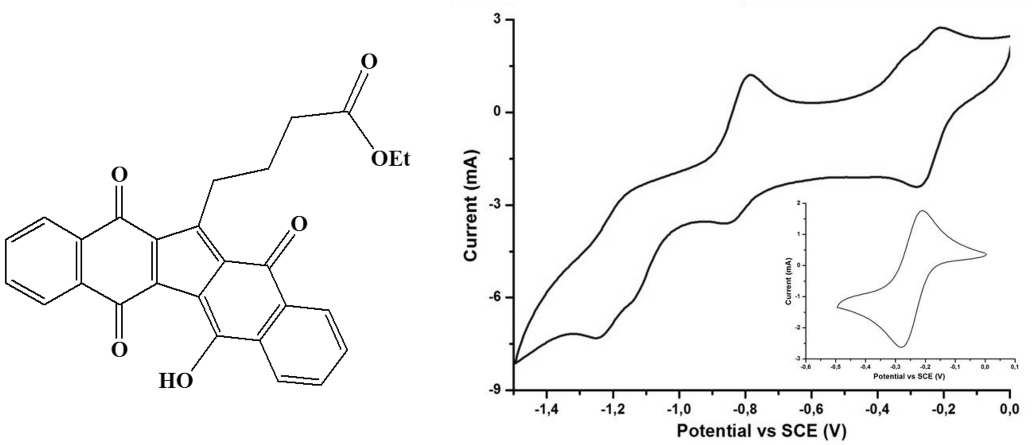

Figure 1: (left) Structure of a KuQ derivate. (right) Cyclic voltammetry of 1-(3-ethoxycarbonylpropyl)KuQuinone.

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Posters

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PO-1

Modified analogues of 4-(2-triethylaminoetiloxy) stilbene as potential selective antagonists of neuronal nicotinic receptors α7

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Nicotine, an unselective agonist of neuronal nicotinic acetylcholine α7 receptors, is able to increase the hyperproliferation of tumour cells [1].

Recent biological assays demonstrated that F1, a potent antagonist of α7 receptors [2], has antiproliferative activity on adenocarcinoma [1] and glioblastoma cell lines. For this reason, F1 and its analogues may be a potential new class of anticancer agents.

Modelling studies suggested that the three substructures of this compound are involved in receptor binding. The aim of this study was the synthesis of F1 analogues modified at the stilbene scaffold in order to increase affinity and selectivity for the α7 receptor, and the investigation of SARs of this substructure.

The first step was the synthesis of α- and β-naphthyl derivatives that incorporate the vinyl linker into an aromatic ring. Subsequently, each benzene ring of the naphthyl moiety was replaced with aromatic heterocycles and therefore the 5-benzofuranyl, 5- and 6-indolyl, benzothiazolyl, benzimidazolyl and benzoxazolyl derivatives were synthesized in order to study other possible interactions with the receptor. All the synthesized compounds were tested for binding affinity to α7 e α3β4 receptors and the SAR at the α7 receptor were supported by modelling studies.

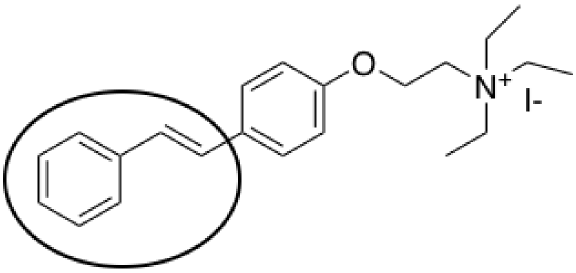

Figure 1. F1.

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PO-2

Synthesis of D-π-A dyes for dye-sensitized photocatalysis

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Dye-sensitized photocatalysis (DSP) is a relatively new approach to convert sunlight into a fuel such as H_2. The required optical and electrochemical properties of the dyes employed in DSP are very similar to those necessary for dye-sensitized solar cells (DSC), including: broad range of absorption in visible λ, high molar absorptivity, efficient electrons injection, stability on multiple red/ox cycles; as a result, the classes of compounds most commonly employed in DSP are those that have shown the highest efficiencies in DSC [1]. Nevertheless, it's still not clear how the dye structure affects the efficiency of catalysis in H_2 production experiments [2]. Thus, the aim of this work is to try to find a reliable guideline for the synthesis of D-π-A dyes with optimized structures for hydrogen production using different Sacrificial Electron Donors (SED).

There are only a few examples in the literature regarding this kind of compounds, none of which contains the 2,1,3-benzothiadiazole moiety, a scaffold that has already shown impressive power conversion efficiencies in DSC [3]. The preparation and spectroscopic/electrochemical characterization of some D-π-A small molecules containing the benzothiadiazole scaffold and featuring an extended conjugation and different electronic properties are reported. The compounds have been designed tuning the photophysical and chemical properties by a proper choice of terminal groups, π-spacers and side chains. All the dyes have been tested in DSSCs and in H_2 production cells leading to interesting results in terms of production rate and TON.

[1] J. Willkomm, L.K. Orchard, A. Reynal, E. Pastor, J.R. Durrant, E. Reisner, *Chem. Soc. Rev.* **45** (2016) 9-23.
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PO-3

FT-IR and LC-DAD-MS/MS for *Cannabis* analysis in (il)legal related products

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Cannabis represents one of the most widely used source of drugs and drugs of abuse worldwide. Its biologically active compounds are cannabinoids, the main ones shown in Figure 1: Δ9-tetrahydrocannabinol (THC, Fig. 1a) to whom the psychoactive effects are attributed, tetrahydrocannabinolic acid (THCA, Fig. 1b), cannabidiol (CBD, Fig. 1c), cannabidiolic acid (CBDA, Fig. 1d) and cannabinol (CBN, Fig. 1e). Together with illegal drugs of abuse (hashish or marijuana) and medical *Cannabis*, some new products have been recently released into the market as legal alternatives as light *Cannabis* variants with low THC content.

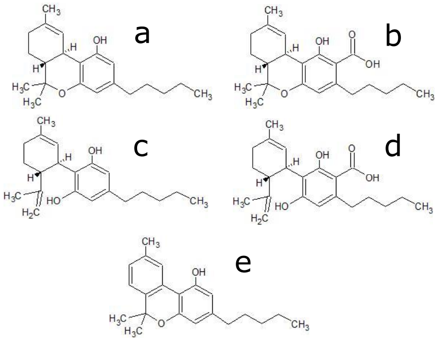

Figure 1. Cannabinoids.

In this research work, some samples belonging to the categories mentioned above were analysed. The analytical approach involved different *Cannabis* products in their commercial (legal) or seized (illegal) forms, without the need for any sample preparation by using an innovative Fourier Transform Infrared (FT-IR) method. The aim was to identify unknown samples, also quantifying their active principles and possible cutting agents/diluents, after development and validation of proper calibration curves. FT-IR results were then compared to those obtained by means of an original LC-DAD-MS/MS method acquiring in multiple reaction monitoring (MRM) mode, through an electrospray ionisation (ESI) source by means of a triple-quadrupole mass analyser, also coupled to a diode array detector (DAD). In addition to the *Cannabis* samples described above, both the IR and LC methods developed in the present work have been applied also to fibre-type plant varieties to monitor the content of non-psychoactive compounds for both pharmaceutical and nutraceutical applications.

This combined strategy of FT-IR and LC-DAD-MS/MS represents an interesting, versatile, fast and reliable tool to assess cannabinoid and related compound levels in regular or illecit samples for quality control and forensic purposes.

PO-4

Multivariate, theoretical and electrochemical approaches to investigate titanium dioxide electrodes in sodium batteries

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Titanium dioxide (TiO_2), in its amorphous as well as most common polyphases including anatase, rutile, brookite and various metastable phases, is under intense investigation as anode candidate for advanced sodium-ion electrochemical energy storage. Na-ion batteries (NiB) are attracting the widespread interest of the scientific community because they may offer the most convenient alternative to current leading-edge Li-ion technology (LiB) for large-scale grid energy storage, where size does not matter and cost, safety and reliability are the most stringent requirements.

In the recent years, various hypotheses have been proposed on the real mechanism of reversible insertion of sodium ions into the TiO_2 structure and literature reports are often controversial in this respect. Interestingly, we experienced peculiar, intrinsically different electrochemical response between amorphous, rutile and anatase TiO_2 nanotubular arrays, obtained by simple anodic oxidation, when tested as binder- and conducting additive-free electrodes in lab-scale sodium cells. To reach deepen insights into the subject, materials were thoroughly characterized by means of scanning electron microscopy and *ex-situ* X-ray diffraction, and the mechanism of sodium ion insertion in the TiO_2 bulk phases was systematically modelled by density functional theory (DFT) calculations.

[1] F. Bella, A.B. Muñoz-García, G. Meligrana, A. Lamberti, M. Destro, M. Pavone, C. Gerbaldi, *Nano Res.* **10** (2017) 2891-2903.
[2] F. Bella, A.B. Muñoz-García, F. Colò, G. Meligrana, A. Lamberti, M. Destro, M. Pavone, C. Gerbaldi, *ACS Omega* **3** (2018) 8440-8450.

PO-5

Regioselective IBX-mediated synthesis of coumarin derivatives with antioxidant and anti-influenza activities

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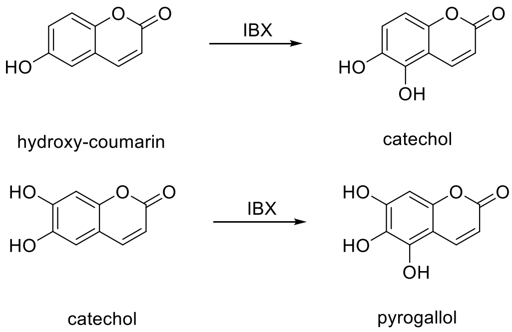
Coumarins are a large class of secondary metabolites found in plants, bacteria, and fungi that showed several pharmacological properties such as anticoagulant, antineurodegenerative, anticancer, antimicrobial, and antiviral activities. In association with these biological effects, coumarins bearing the catechol pharmacophore (Scheme 1) are potent antioxidants in lipid peroxidation, H_2O_2-induced oxidative cell damage, and glutathione (GSH) depletion. This antioxidant activity is associated also with inhibition of specific classes of virus, such as Influenza A virus, particularly sensitive to the intracellular redox equilibrium [1]. In order to evaluate the role of the oxidation state of coumarins in antiviral activity, we regioselectively synthesized a library of new coumarin derivatives bearing catechol and pyrogallol moieties by the use of 2-iodoxybenzoic acid (IBX) (Scheme 1) [2]. This library of catechol and pyrogallol derivatives, showed improved antioxidant effects in the DPPH test and inhibitory activity against the influenza A/PR8/H1N1 virus [2]. These data represent a new entry for highly oxidized coumarins showing an antiviral activity possibly based on the control of the intracellular redox value.



Scheme 1. General structures of the library synthesized.

[1] D. Amatore, R. Sgarbanti, K. Aquilano, S. Baldelli, D. Limongi, L. Civitelli, L. Nencioni, E. Garaci, M.R. Ciriolo, A.T. Palamara, *Cell Microbiol.* **17** (2015) 131-145.
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PO-6

Origami multiple paper-based electrochemical biosensors for pesticide detection

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Pesticides are largely used at worldwide level to improve the food production, fulfilling the needs of the global population, which is increasing year by year. Although persistent pesticides (e.g. DDT) have been replaced with less persistent ones, contamination of food, soil and water by pesticides remains an issue of public concern. To better manage this problem, EU sets regulations for a sustainable employment of pesticides by promoting the adoption of Integrated Pest Management (Directive 2009/128/EC) [1]. The criticism on pesticides is also highlighted in the frame of European Water Policy (Directive 2008/105/EC) [2]. In this overall scenario, the detection of pesticides in water at low concentrations (ppb level) is required to accomplish the regulatory aspect and to preserve the health of environment and human being.

Herein, we propose the first three-dimensional origami paper-based device for the detection of several classes of pesticides by combining different enzyme-inhibition biosensors. This device was developed by integrating two different office paper-based screen-printed electrodes and multiple filter paper-based pads to load enzymes and enzymatic substrates. The versatile analysis of different pesticides was carried by folding and unfolding the filter paper-based structure, without any addition of reagents and any sample treatment (i.e. dilution, filtration, pH adjustament) [3]. The paper-based platform was employed to detect paraoxon, 2,4-dichlorophenoxyacetic acid, and atrazine at ppb level in both standard solutions and river water sample, by exploiting the capability of these different types of pesticides (i.e. organophosphorus insecticides, phenoxy-acid herbicides, and triazine herbicide) to inhibit butyrylcholinesterase, alkaline phosphatase, and tyrosinase, respectively. The degree of inhibition correlating to the quantity of pesticides was evaluated by chronoamperometrically monitoring the enzymatic activity in the absence and in the presence of pesticides by using a portable potentiostat. To improve the sensitivity, the paper-based electrodes were modified with carbon black alone in the case of platforms for 2,4-dichlorophenoxyacetic acid and atrazine detection or decorated with Prussian blue nanoparticles for the detection of paraoxon.

The accuracy of this origami multiple paper-based electrochemical biosensor was evaluated in river water by recovery studies, obtaining satisfactory values (e.g. for paraoxon 90 ± 1% and 88 ± 2%, for 10 and 20 ppb, respectively). The proposed three-dimensional origami paper device allows for rapid, cost-effective and accurate pesticide detection in surface water as a result of combining filter and office papers, screen-printing, wax-printing and nanomaterial technology.

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[2] Directive 2009/128/E.
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PO-7

Design, synthesis and evaluation as potential pharmacological chaperones for Gaucher disease of 2-substituted trihydroxy piperidines

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A set of 2-substituted trihydroxy piperidines was designed, synthesized and evaluated as potential Pharmacological Chaperones for Gaucher disease (GD). GD is the most common autosomal recessive lysosomal storage disorder caused by point mutations in the gene encoding acid-β-glucosidase (β-GCase), enzyme responsible for glucosylceramide metabolism into glucose and ceramide. One approach to treat this disease is to use pharmacological chaperones, which are small-molecules that bind to and stabilize misfolded proteins able to restore its catalytic activity, if used in sub-inhibitory amount [1,2]. The synthetic strategy to obtain 2-substituted trihydroxy piperidines is disclosed. This strategy allows the introduction of different alkyl groups at C-2 position of the piperidine, obtaining 2-substituted piperidines with both configurations at the newly formed stereocenter bearing an hydrophobic chain to mimic the enzyme natural substrate. The strategy involves Grignard addition onto a carbohydrate derived nitrone and an efficient ring-closure reductive amination strategy in the final cyclization step [3]. Biological evaluation of these new 2-substituted piperidines will be also presented. They were screened as GCase inhibitors and the most promising inhibitors were tested as PCs in fibroblasts from GD patients.

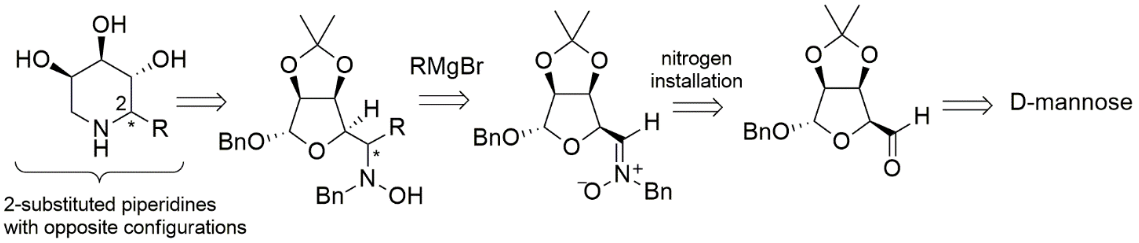

Figure 1. Retrosynthetic strategy to access 2-substituted piperidines.

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[2] P. Compain, O.R. Martin, *Iminosugars: From Synthesis to Therapeutic Applications, Wiley VCH*, New York (2007).
[3] S. Mirabella, G. Fibbi, C. Matassini, C. Faggi, A. Goti, F. Cardona, *Org. Biomol. Chem.* **15** (2017) 9121-9126.

PO-8

Synthesis and investigation of croconates as smart organic coating for noble metals nanoparticles

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Croconic acid is a cyclic organic molecule, belonging to a particular family of compounds called oxo-carbon acids. This molecule properly functionalized exhibit an absorption in NIR region and this property can be exploited in the design of NIR-harvesting materials obtained with a hybridization of a nano-material, characterized by a NIR absorption, with this organic molecule.

The purpose of this research is to combine a particular type of gold nanoparticles, called nanorods (AuNRs), with a specific aspect ratio (AR) in order to have an absorption in NIR region (900-1100 nm), with a croconic acid. This latter must be properly functionalized with an alkyl spacer (for example thiol-ending) in order to allow the anchoring to the AuNRs.

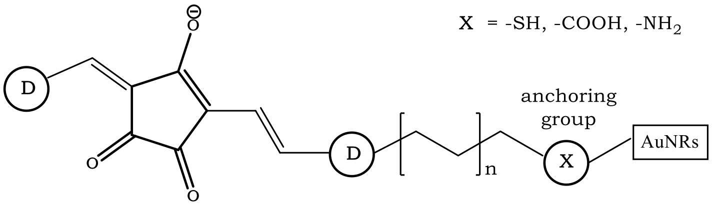

Figure 1. NIR-harvesting material.

Croconic acid absorption in the IR region can be tuned by varying donor moieties. Some experiments reported in the literature have revealed that increasing the conjugation in the donor part of the croconic unit leads to a red shift in NIR region (~1000 nm).

Croconic acid is synthetized following the method reported by Fatiadi et al. [1]. For the synthesis of gold nanorods the Seed-Mediated Growth method is followed [2].

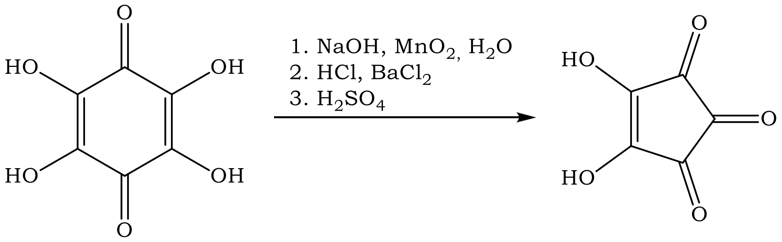

Figure 2. Croconic acid synthesis.

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PO-9

Recovery and recycling for a sustainable future in the chemical industry

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Circular economy suggests an innovative way of exploiting resources that is only viable through closed industrial loops. The recovery and recycling of building blocks, semi-finished products and waste streams guarantee the possibility of exploring new businesses by reducing the environmental burdens due to extraction and refining of virgin materials. This approach can be realized through a new way of thinking, based on the waste-to-resource opportunity. As a matter of fact, the core principles of the circular economy involve the recycling and the re-use of materials accompanied by a holistic and sustainable use of resources [1]. Clark et al. [2] introduced a new strategy to drive innovation with a sustainable utilization of resources: the so-called concept recirculation. A recirculated product should be returned back to a usable state without becoming waste. By this way, the researchers can maximize material efficiency by reducing pollution and potential toxic effects.

In this work we briefly discussed the importance of recycling within the chemical sector and we reported on some recent examples of strategies helpful to minimize waste by increasing the efficiency of the whole system and promoting a greener/safer chemical industry [3].

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[2] J. Sherwood, J. Clark, T. Farmer, L. Herrero-Davilla, L. Moity, *Molecules* **22** (2017) art. no. 48.
[3] R. Cucciniello, D. Cespi, *Recycling* **3** (2018) art. no. 22.

PO-10

Synthesis of dopant-free polymers for perovskite solar cells

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The increasing world energy demanding makes compulsory the search of energy sources alternative to fossil fuels. Among alternative energy source, the solar energy is green, renewable and not exhaustible. Perovskite Solar Cells (PSC), which rose in efficiency from the 3.2% (2012) to 22-23% in only 5-6 years[1], are the new frontier of the photovoltaic research. The perovskite crystals are the core of the device, giving easy charge separation and high charge mobility. The two sides of the perovskite layer are covered with an Electron Transport Material (e.g. TiO_2, n-doped semiconductors…) and a Hole Transport Material which drain charges efficiently. Unfortunately, perovskites show instability towards moisture, which rapidly deteriorates the device performances. The use of polymeric HTMs layers on one perovskite side seems to overcome those problems, granting a good stability increase, since the optimal filming properties of hydrophobic polymers.

Most HTMs need to be doped to show good conductivity levels, useful for PSC cells, but doping agents are detrimental for cell stability since they are hygroscopic and, through them, water can reach the perovskite layer. Recently, we prepared P3HT and PTAA but now we are interested into polymeric HTMs showing an inherent high conductivity, which became the next HTM research topic, the "dopant-free" conductive polymers [2]. To prepare a promising dopant-free polymer, a donor-acceptor monomer (**1**) was prepared by Suzuki coupling on a dibromoaldehyde derivative, followed by Knoevenagel condensation with malonitrile under microwaves. The final polymerization using $FeCl_3$ gave a red colored polymer (**2**).

Besides usual synthesis, the synthesis of intermediates and final polymers will be also addressed in micellar media, a Green Chemistry technique [3].

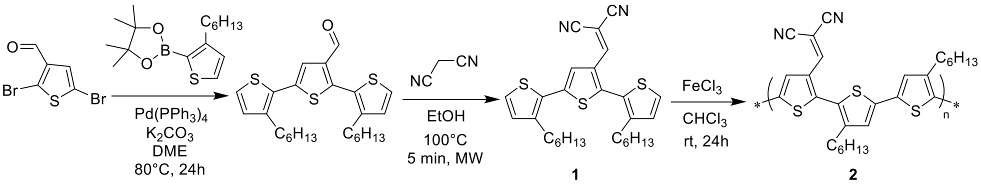

Figure 1. Synthesis of the donor-acceptor conductive polymer.

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PO-11

Determination of heavy metals in cosmetic products

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The REACH regulation and the European cosmetics legislation (Regulation No 1223/2009/EC) prohibit the use of heavy metals in final products, but tolerate their presence in traces providing that it is technically unavoidable. Despite the observance of Good Manufacturing Practices (GMP), their presence in the final product is possible. Nevertheless, the final cosmetic products must be safe for human health.

The prohibition of the use the metals with known or suspected toxicity as ingredients in cosmetics and equally acceptance of their presence in traces, implies an ambiguity in the European regulation.

The main difficulty to set out well-defined metal concentration limits is due to their presence in various and complex cosmetic matrices.

The purpose of the research is the comparison of analytical data collected on cosmetic samples with different matrices (creams, oils, perfumed water, sun oils but also toothpastes, soaps, shaving soaps, shampoos, balms) in order to highlight the amount of metals in the samples. In addition a comparison of different analytical methods was performed. For this purpose, about 100 samples of traditional and organic cosmetics were analyzed to quantify Al, Ag, Cr, Cd, Ni, Pb and Zn. The matrices were treated by two different methods of mineralization: (i) wet digestion and/or incineration and (ii) the microwave assisted digestion using closed vessel in microwaves.

Above mentioned methods, the most effective method was the microwave assisted digestion. The metal content is generally low despite of the limits imposed by the Italian Higher Institute of Health (ISS).

Moreover, it was also possible to draw a trend on the prevalence of some metals according to different types of cosmetics.

In conclusion, the evaluation of metals in cosmetics is fundamental to overcome the ambiguity in the REACH regulation, trusting in a future correction of the normative text to protect consumers.

[1] Regulation (EC) No 1223/2009 of the European Parliament and of the Council.
[2] B. Bocca, R. Briancesco, I. De Angelis, R. Porrà, Giornata informativa sui prodotti cosmetici. Aspetti regolatori e problematiche emergenti, ISSN:1123-3117.

PO-12

Enhanced biostability and biocompatibility of zinc oxide nanocrystals shielded by a phospholipid bilayer

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In recent years many efforts have been devoted to study zinc oxide nanocrystals (ZnO NCs) as diagnostic and therapeutic tools, in particular for cancer treatment. Those nanostructures show interesting cytotoxic properties and can be easily synthesized and functionalized, with the purpose of improve their biocompatibility and selectivity [1]. However, in order to enable the use of ZnO NCs for clinical applications, a better control of their stability in the biological environment is required. In particular, the issues to be addressed are the aggregation and dissolution of nanocrystals and their interaction with the components of the biological media, all parameters that can affect the NCs bio-distribution, and cytotoxicity [2].

In this scenario, we decide to evaluate the colloidal stability and the long-term biodegradation behavior of synthesized ZnO NCs as a function of their surface functionalization. In particular, we propose to modify the surface of pristine ZnO NCs with a biomimetic phospholipid shell, constituted by self-assembled liposomes [3] or cell-derived extracellular vesicles, in order to promote the stability and biocompatibility of the nanocrystals in the physiological environment. The stability tests, performed in multiple biological media, demonstrate that pristine ZnO NCs rapidly aggregate in complex biological media while long-term assessments show that this aggregation is accompanied by a small dissolution into potentially cytotoxic Zn^{2+} cations and a slight alteration of NCs surface and crystalline structure.

In contrast, the encapsulation of ZnO NCs in a lipid layer, leads to NCs with better colloidal stability and chemical resistance in the biological environment. In addition, the biological nature of the cell-derived vesicles allows to improve the biocompatibility, making our hybrid nanoconstruct a promising candidate for theranostic applications.

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PO-13

Reversible energy transfer to lanthanoid ions mediated by calixarenes

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Massimiliano Massi,[b] and Francesco Sansone[a]

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The near infrared emission of lanthanoid ions is highly sought after for a number of applications including biological imaging and sensing, night vision displays as well as telecommunication signalling [1]. Previous work in this area investigated the binding and sensitisation of visible emitters such as trivalent Eu, Tb, and Sm to calix[4]arene scaffolds functionalised on the lower rim by three amide groups [2]. The sensitisation originated from electronic transitions occurring on the aromatic rings of the calix[4]arene structure. However, the process was found to be inefficient due to an energy mismatch between the triplet excited state of the ligand and the 4f* accepting state of the lanthanoid ions [3]. Furthermore, very limited energy transfer was observed for complexes formed with near-infrared emitting lanthanoid ions, such as Er, Nd, and Yb.

We report here our work towards improving the near infrared emission of calix[4]arene/lanthanoid ion complexes by covalently grafting a suitable antenna to the lower or upper rim of the calix[4]arene systems (Figure 1). Possible antennae include naphthalimide and flavin-based components.

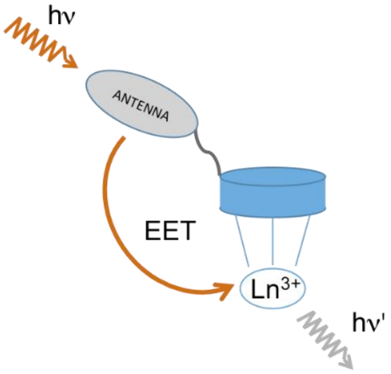

Figure 1. Schematic representation of a generic calix[4]arene/antenna system for the sensitization of lanthanoid ions.

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PO-14

Open innovation at De Nora

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De Nora (www.denora.com) is a global company leader in the manufacture and supply of components for the electrochemical industry and in the development of water and wastewater treatment solutions.

Founded by Ing. Oronzio De Nora in 1923, the company became soon a top-level supplier of chlor/alkali plants and components for the electrochemical industry.

Today, De Nora serves most of the electrochemical industry with electrodes and electrochemical cells, owning the majority of the market share in chlorine and caustic production, surface finishing, plating for printed circuits, cathodic protection, industrial and pools disinfection. More recently, De Nora became one of the leaders worldwide in the supply of complete solutions for municipal, industrial and marine water/wastewater treatment applications.

Thanks to its highly qualified R&D team, located in Italy, USA and Japan, De Nora can provide short- and long-term solutions for a great portfolio of industrial applications.

Recently, a global open innovation (OI) function has been created, with the goal to support the whole Company, starting with all the R&D teams, by establishing a growing network of industrial and academic partners.

In this poster contribution, the open innovation paradigm [1] is presented along with a description of its implementation at De Nora. In contrast with the traditional model of innovation, which is internally focused, open innovation strategically leverages internal and external sources of ideas and takes them to market through multiple paths.

The main activities of the OI function involve scouting for novel technologies, collection and analysis of technology-related information, seeking opportunities of licensing and acquisition, as well as participation to consortia, such as the VoltaChem program, a publicly-funded innovation program for the electrification of the chemical industry.

[1] H.W. Chesbrough, *Open Innovation: The New Imperative for Creating and Profiting from Technology*, Harvard Business School Press, Boston, 2003.

PO-15

Development of a new HPLC-ESI-MS/MS method to profile bile acid metabolism oxidation products in human feces

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Bile acids (BAs) are endogenous steroids involved not only in the transport of lipids in the enterohepatic circulation but acting as molecular signalling hormones [1]. Primary BAs synthesized in the liver undergo several metabolic pathways in the intestine by gut microbiota to produce secondary BAs. Beside secondary BAs, other metabolites have been recovered from human feces [2]; among these, many oxo-BA analogues are produced in the colon through oxidation of BA hydroxy groups. Some reports have shown their ability to interact with enzymes and receptors as classical BAs [3].

With this aim, we developed a new validated reverse phase (C18 column) HPLC-ESI-MS/MS method in negative ionization (MRM) for the analysis of up to 21 oxo-BAs in human feces. This method also included the separation of the BA precursors, in order to achieve a comprehensive simultaneous evaluation of these compounds. The elution was accomplished in gradient mode and an overall of 28 compounds, including primary, secondary BAs and their oxo-derivatives, were separated within 40 minutes at 40 °C column temperature. The method is accurate (bias%<10%), precise (CV%<10%) with limit of quantification (LOQ) <10 nM, similar for all the studied compounds. Matrix effect does not affect significantly the analysis accuracy, allowing the use of calibration curves in mobile phase, without any matrix-matched protocols.

The method was used to analyze oxo-BAs in human fecal samples from healthy subjects to define the most representative and their potential involvement in intestinal diseases as well as potential signaling molecules.

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PO-16

Synthesis and characterization of polymethacrylates functionalized with azocompounds for 3D printing

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Three-Dimensional-Printing (3DP) has been introduced in the late 80s and, nowadays, it is recognized as one of the most promising and revolutionary manufacturing technologies. The exploration of innovative functional materials along with the corresponding 3DP is constantly growing to fulfill the ever-increasing market manufacturing demand [1]. Typical examples of smart polymers deeply investigated in 3DP are temperature-, light- and pH-responsive, and mechanochromic materials. Among many monomers, azo-based scaffolds have been reported to provide well-defined either photohardening or photosoftening 3D devices under laser irradiation [2].

We have designed, synthesized and characterized functional polymers defined by one or more smart properties along with specific Additive Manufacturing (AM) compatibility. In particular, polymers bearing dye-functionalized polyacrylates or polymethacrylates can be developed in a straightforward manner for both Digital Light Processing (DLP) and Stereolithographic Apparatus (SLA). Azobenzene-based monomers used are both suitable candidates, thanks to their high speed of light curing, for the 3DP-light responsive polymers preparation, conferring potential light triggerable-mechanical responses, due to the *trans-cis* isomerization upon UV irradiation. Furthermore, the different ortho group confers various properties due to both steric and electronic effect.

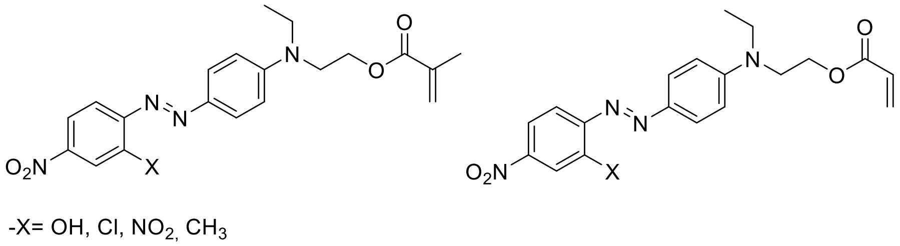

Figure 1: Structure of monomers.

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PO-17

Cocoa shell waste valorization – extraction from lab to pilot-scale cavitational reactors

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The objective of the presented study is to valorize cocoa shell, one of the main by-product of the roasting process, in order to enhance the effective extraction of high value-added compounds by means of sustainable protocols. Aiming to define the best solvent and technology, a range of extraction procedures have been tested. Used solvents were hexane, hydro-alcoholic solution (ethanol/water) and ternary mixture (hexane/ethanol/ water). Ultrasound (US) and hydrodynamic cavitation (HC) were compared with conventional methods. High temperature and pressure microenvironments generated by cavitation promote fast biomass deconstruction with low energy consumption [1]. The optimized protocol combine a pilot flow HC reactor with a ternary mixture, simultaneously providing a hydrophilic product, which is rich in polyphenols and methylxanthines, and a lipid layer. Sequential milling and sieving pretreatment provided an enriched cocoa shell fraction trough the partial removal of husk fibers (54.45 vs. 81.36 w/w % total fibers). The disposal of the fibers reduces mass balance, but they can be applied as animal feedstock components and crop mulching. The aforementioned protocols produce valuable extracts, which are rich in flavanols (catechins and epicatechins), theobromine, caffeine and cocoa butter, in a simple and easy manner. This valorization process provided 20.5 % (w/w) and 15.8 % (w/w) hydrophilic and lipophilic fractions, respectively. The hydrophilic extract shows an extremely high total phenolic content of 197.4 mg/g extract (gallic acid eq.), with a radical scavenging activity of 62.0 ± 3.1 μg/mL (expressed in DPPH EC50). The fatty acids, obtained in a great yield (forming the 96.4 % (w/w) of the total lipophilic fraction) well match the commercial cocoa butter profile. These results run in the direction of zero waste chocolate industry by means of low cost, fast, efficient and scalable procedures [2].

[1] F. Chemat, M. Abert-Vian, G. Cravotto, *Int. J. Mol. Sci.* **13** (2012) 8615-8627.
[2] G. Cravotto, F. Mariatti, V. Gunjevic, M. Secondo, M. Villa, J. Parolin, G. Cavaglià, *Foods* **7** (2018) art. no. 130.

PO-18

Chemoinformatics analysis of the molecular diversity of an in-house library of morpholine peptidomimetics

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Modern chemical biology requires efficient synthetic processes, able to produce high-quality small-molecule collections, as probes to investigate biological pathways [1]. Our efforts in this field are focused on the generation of different peptidomimetic compounds around the morpholine nucleus, heterocycle contained in many different bioactive molecules, by using different build/couple/pair strategies, able to increase the sp^3-character and the molecular complexity of the structures. In this work, an in-house library of 183 different morpholine-derived small molecules (see Figure 1a for some representative examples) has been evaluated following Lipinski rules (Figure 1b); and analyzed in terms of shape and chemical properties using PCA (Principal Component Analysis) and PMI (Principal Moment of Inertia) analysis (Figure 1c) [2].

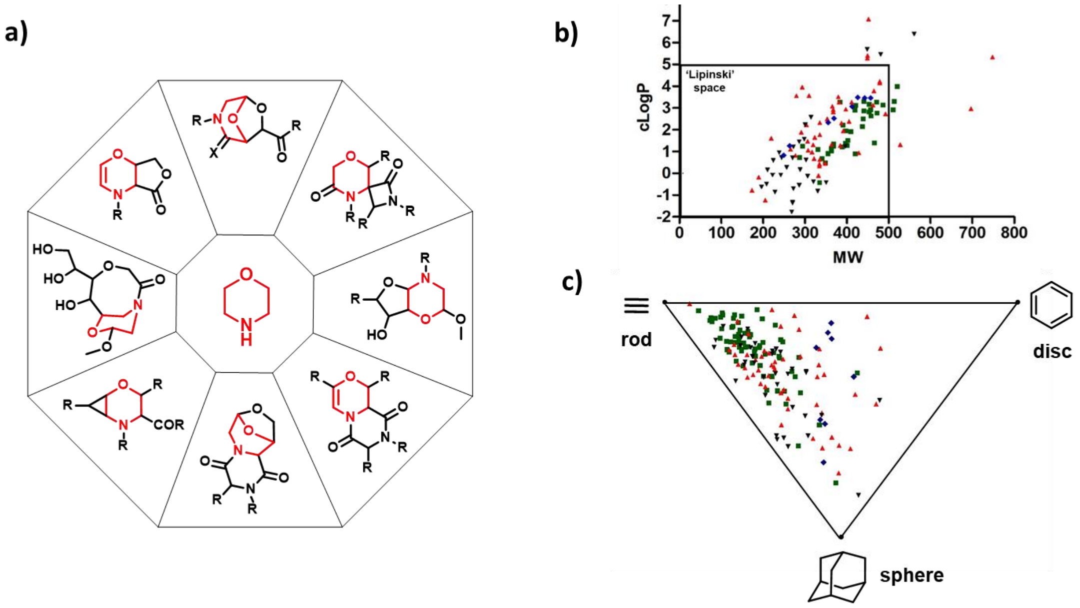

Figure 1: (a) Representative examples of morpholine-derived molecular scaffolds; (b) physical chemical properties (clogP versus molecular weight) and (c) PMI shape analysis of the 183 morpholine-derived small molecules.

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PO-19

New phosphine/diimine ruthenium(II) complexes as promising anticancer agents: cytotoxicity and pro-apoptotic activity

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Nowadays many metal compounds are widely used in medicine as therapeutic and diagnostic agents (contrast agents, radiopharmaceuticals, antitumor drugs). Due to their versatile biochemical properties, ruthenium-based compounds have shown to be promising anti-cancer agents as alternatives to cisplatin and its derivatives, which produce non-cancer cell toxicity causing severe adverse effects, although they are efficacious against the vast majority of cancers [1].

Our work is focused on the synthesis and characterization of new ruthenium(II) complexes of general formula *cc*-[Ru(X)(CO)(PP)(diimine)]X, [X = anionic ligand; PP = diphosphine; diimine = 2,2′-bipyridine or 1,10-phenanthroline] [2] which are tested *in vitro* for their anticancer activity by means of MTT and apoptosis assays against selected cancer cell lines, reaching very low values of IC_{50}. In this study, we also expect that these cytotoxic drugs will be selectively transported into cancer cells with the help of biomolecules in specific cancer conditions.

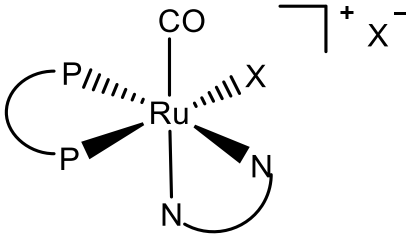

Figure 1. cc-[Ru(X)(CO)(PP)(diimine)]X.

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[2] M.I.F. Barbosa, R.S. Correa, T.M. Bastos, L.V. Pozzi, D.R.M. Moreira, J. Ellena, A.C. Doriguetto, R.G. Silveira, C.R. Oliveira, A.E. Kuznetsov, V.S. Malta, M.B.P. Soaresch, A.A. Batista, *New J. Chem*. **41** (2017) 4468-4477.

PO-20

Organo-modified nanoclays for composite gel polymer electrolytes in lithium-ion battery: a study of ionic transport and mechanical properties

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A series of composite gel polymer electrolytes (GPEs) have been prepared and investigated. The nanocomposites were based on organo-modified montmorillonite (MMT) clays obtained after intercalation of CTAB molecules in the interlamellar space of sodium montmorillonite (Na-MMT) through a cation-exchange reaction. The functionalized clay was then used as nanoadditive in polyacrylonitrile (PAN)/polyethylene-oxide (PEO) blend polymer, lithium trifluoromethanesulphonate (LiTr) as salt and a mixture of ethylene carbonate/propylene carbonate as plasticizer. All the GPEs were investigated by thermal (DSC), morphological (scanning electronic microscopy-SEM) and mechanical (DMA) analysis, while the ion transport studies were conducted by electrochemical impedance spectroscopy (EIS) and by multinuclear NMR spectroscopy.In particular, NMR spectroscopy has been widely applied in order to directly investigate the molecular dynamics of the cation (^{7}Li) and anion (^{19}F) through the analysis of self-diffusion coefficients (Pulse Field Gradient –PFG method) and the spin-lattice relaxation times (T_1) (inversion recovery sequence). The combination of the electrochemical and NMR data has provided a wide description of the ions dynamics inside the so complex systems, as well as information on ion associations and interactions between polymers, filler and ions.

PO-21

Miniaturised sample pre-treatment and LC-MS/MS analysis of artemisinin in plant extracts and supplements

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Sweet wormwood or sweet annie (*Artemisia annua* L.) is a small annual plant of the Asteraceae family, which has been in use for centuries in traditional medicine for the treatment of fever, including fever originating from malaria. The main active principle of *A. annua* is artemisinin, which is currently acknowledged as one of the most effective drugs in antimalarial therapy. Aim of the present study is the development and application of an original procedure for the LC-MS/MS analysis of artemisinin after miniaturised pre-treatment of sweet wormwood plant extracts and supplements prepared form the plant.

Microextraction by Packed Sorbent (MEPS) was chosen for sample pre-treatment; it is a miniaturised version of solid-phase extraction (SPE) that provides lower solvent and sample consumption, easier and cheaper automation and equivalent performances [1]. The developed pre-treatment procedure uses a C8 sorbent and requires just 100 μL of sample (fluid extract from plant or supplement). The methanolic eluate was pre-concentrated and analysed by means of an original, validated LC-MS/MS method, using deuterated artemisinin as the IS. The method provides good linearity in the 5-1000 ng/mL concentration range, extraction yields in the 85-90% range and good precision.

Application of the MEPS procedure and LC-MS/MS method to plant extracts and supplements provided sound results. Both handmade and commercial preparations contained artemisinin amounts compatible with the expected or declared composition, ranging from a few micrograms per millilitre to hundreds of micrograms per millilitre. Despite the limited analyte stability, no sign of degradation was found during the analytical procedure.

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PO-22

Synthesis of a new artificial linker resorc[4]arene-based system for protein immobilization

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One of the main problems in the development of immunosensors is to overcome the complexity of binding antibody to the surface of the sensor.

In fact, antibodies need to be immobilized with a high density and good orientation to allow the easy detection of antigens and for the improvement of the performance enhancement.

Resorc[4]arene derivatives have been proposed as an alternative tool for the oriented immobilization of antibodies thanks to their particular structure of lower and upper rims which can be modified to bind specific guest molecules [1].

We synthesized several resorc[4]arene derivatives able to self-assemble onto gold surface thanks to the thio-ether groups present on their structure (see figure below) [2]. The immobilization characteristics of these artificial linkers have been evaluated by means of Surface Plasmon Resonance (SPR) technique comparing the results obtained with a random immobilization method based on EDC/NHS and boronic acid derivatives of insulin antibody for the development insulin immunosensors. These compounds show an enhancement of the insulin-insulin antibody interaction, resulting in a significative increase of the immunosensor sensitivity.

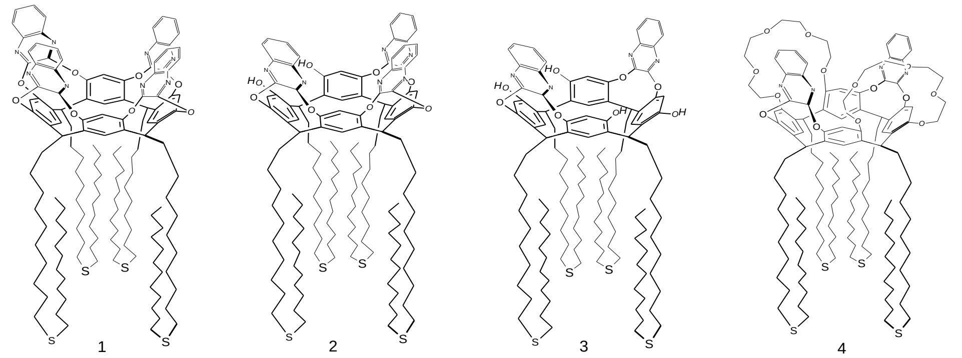
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Figure 1. Resorc[4]arene linkers.

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PO-23

Renewed PVC: new recycling strategies

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The PVC global consumption is about 35 million tons/year and constantly increasing, of which only around 16% is recycled (VinylPlus-Progress Report 2017). The main problems related to PVC recycling are the high chlorine content, which may lead to the release of HCl and dangerous materials, and difficulties in predicting upstream the real composition of the material, due to the several additives added and post-consumer residuals [1,2].

The aim of this work is then the development of new strategies of recycling and/or reusing waste polyvinylchloride (W-PVC) recovered from electric cables by R.ED.EL. Srl (Figure 1).

Firstly, the amount of HCl released has to be evaluated: for this purpose, a new methodology was developed, consisting of an acid-base titration of water-dissolved evolved-gas in a temperature range of 25-350°C. The results were compared with those of TG analysis. That last showed that the dehydrochlorination process starts at 130°C, with a maximum at 205°C and a weight loss equal to 19.77%, while the titration demonstrated that just 1.05% of the evolved-gas is HCl.

The subsequent complete physicochemical characterization of the W-PVC will allow to develop and/or optimize mechanical recycling, by testing it in composite materials, and chemical recycling, by means of catalytic pyrolysis mediated by zeolite, in order to convert the W-PVC in advanced biofuels.

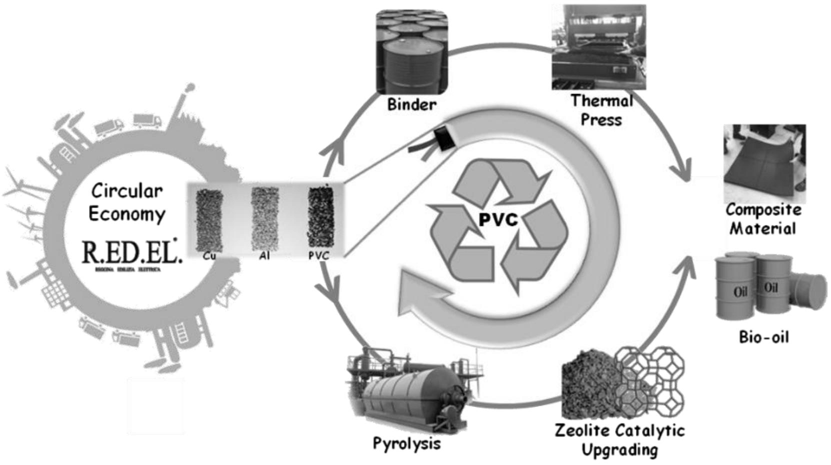

Figure 1: Representation of the Zero Waste Program.

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[2] L. Ciacci, F. Passarini, I. Vassura, *Resour. Conserv. Recy.* **123** (2017) 108-116.

PO-24

Preparation and synthetic applications of a new class of α-nitro functionalized enolates

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Enolates are the anions of enols and are characterized by two resonance structures in which the negative charge is delocalized on the carbon or oxygen atoms.

The delocalization of the charge allows the C- or O-alkylation depending on reaction conditions and, for this reason, they have been widely involved in a huge number of synthetic processes such as: additions, coupling and hydrogenation reactions. Enolates could be divided in two classes: (i) unstable enolates, generated in situ and directly suitable for the appropriate reaction and, (ii) stable enolates that can be isolated and stored. Metal enolates, such as the lithium and magnesium ones belong to the first class, while silyl enol ethers and acyl enolates belong to the second class. In this work we have (i) implemented a new synthetic strategy (Fig. 1) for preparing a new class of enolates, namely the a α-nitro functionalized enol acetates, and (ii) explored their reactivity due to the presence and peculiarities of enolate and nitro groups.

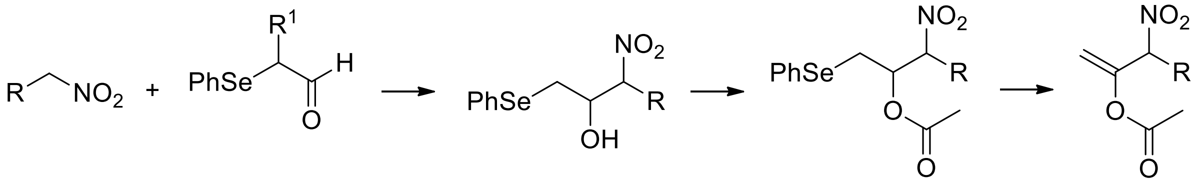

Fig. 1. The synthetic pathway for the preparation of the new class of enolates.

PO-25

Color prediction of flexible dyes in aqueous solution: a combined MD/QM approach

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The accurate prediction of spectral features determining the color of dyes in complex environment represent a challenge for industrial research. Setting-up a computational protocol allowing to quantitative simulation of the perceived color would provide a cost-effective alternative to the synthesis and characterization of new compounds, enabling the design of new dyes with customized properties within shorter time scale.

For structurally rigid dyes a theoretical protocol based on a quantum mechanical description in the framework of Time-Dependent Density Functional Theory (TDDFT) in implicit solvent environment allows the prediction of the absorption band shape and position since for such systems the vibronic coupling based on the Frank Condon assumption is expected to be a valid model [1]. While the simulation of flexible dyes optical properties requires efficient protocols able to explicitly account for the intrinsic complexity of both solute and solvent. Therefore, a model that explicitly takes into account the environment embedding the solute has to be considered. A procedure based on combination of molecular dynamics (MD) and quantum mechanical (QM) approaches represent the most promising strategy to reach this aim [2-3].

In this work, the spectroscopic properties of various flexible dyes in aqueous solution have been investigated through a theoretical approach combining a classical MD sampling of the whole system, by using a non-reparametrized force field, with TDDFT calculations of the dye under investigation. The QM calculations have been performed on representative snapshots, chosen as function of the selected degree of freedom, taking into account the solvent effects using an implicit model (PCM). The final spectrum is achieved weighing each vertical transition with a Boltzmann distribution.

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PO-26

Revealing the nature of the interaction between a novel TF-Thr mimetic with Gal-3

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Mucins are high molecular weight glycoproteins largely expressed by endothelial cells. They represent a physical protection for organs, against harmful species. When normal mucin becomes tumoral, a pathological oversimplification of the glycosidic portions occur and saccharides, normally hidden, become exposed (identify as tumoral marker). Galectins are a family of proteins characterized by specific recognition domains for carbohydrates (Carbohydrate Recognition Domain, CRD) [3] and with high affinities for β-galactosides epitopes. The most studied galectins are Gal-1 and Gal-3 and in particular, Gal-3 plays a fundamental role in tumoral progression which is known to be mediated by the binding with TF antigen [1]. TF and Tn antigens are examples of mucin associated carbohydrate antigens, highly expressed in many tumors but practically absent on healthy cells. They are linked by an α-O-glycosidic bond with a serine or threonine residue to the mucin's peptide backbone. Due to their almost exclusive presence on cancer cells, these antigens are interesting targets for the development of therapeutic cancer vaccines. Recently, we have developed a mimetic of Tn-Thr antigen [2] and relying on previous results, we have developed and optimized the synthesis of a TF-Thr antigen mimetic. In collaboration with the University of Lisbon were performed X-ray crystallography, NMR binding studies and isothermal calorimetry assays to unravel the molecular structural issues that govern the Gal-3/TF-Thr-mimetic interaction [3].

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[2] J. Jimenez-Barbero, E. Dragoni, C. Venturi, F. Nannucci, H.J. Gabius, A. Ardá, M. Fontanella, S. André, F.J. Canada, C. Nativi *Chem. Eur. J.* **15** (2009) 10423-10431.
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PO-27

Benzo-bisthiazole derivatives: a new class of green/yellow emitting fluorophores for luminescent solar concentrators

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The direct conversion of the solar energy in electricity of the PV devices, the elevated costs of the materials and the building integration problems limited the large diffusion of this devices. For this reason, research on new tecnologies leads on cheaper and less impactfull devices than PV panel. In this context, Luminescent Solar Concentrators (LSCs) appear a promising concept. We developed new flurophores with a benzo[1,2-*d*:4,5-*d'*]bisthiazole heterocyclic unit as π bridge with a different D-π-D structure.

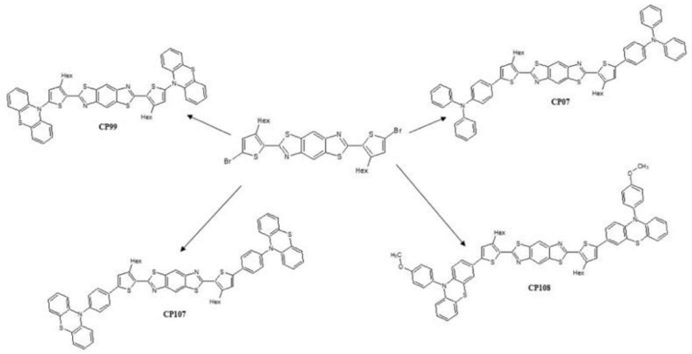

Figure 1. Benzo-bisthiazole derivatives synthetized.

The new compounds displayed light absorption in a range of 400-500 nm and an emission at 550-600 nm. The dyes showed a good Stokes shif and a good Φ. In particular, CP07, with a large Stokes shift (92 nm) and a high quantum yield (0.68), was employed in the development of LSC device, provided a remarkable optical efficiency at the highest concentration tested (6.42% at 1.4%wt) [1].

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PO-28

Electrospun polyvinylpyrrolidone for soundproofing

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Noise pollution is a remarkable problem in modern society and can constitute a real risk to the human health.

Non-woven light (density = 63 Kg/m^3) soundproofing materials were successfully obtained by electrospinning polyvinylpyrrolidone (PVP) of high molecular weight (1300 kDa). The sound absorber were produced as thin disks of 10 cm in diameter with a fiber diameter of (1.6 ± 0.5) or (2.8 ± 0.5) μm [1]. PVP samples show better sound absorption properties in the lower frequency range when compared with materials of same thickness that are commonly used in engineering fields.

The sound absorption coefficient α_a, for a set of blankets (from a minimum of 6 disks), changes in the frequency range 250–1600 Hz following a bell-like curve trend with the maximum (where α_a is close to 1.0) that shifts to lower frequencies by adding piled disks. The acoustic behavior can be, therefore, continuously tuned by changing the mass of the blanket.

The experimental results suggest that sound energy dissipation occurs when the sound wave is resonant with the natural vibration frequency of the blankets pile like a membrane [1].

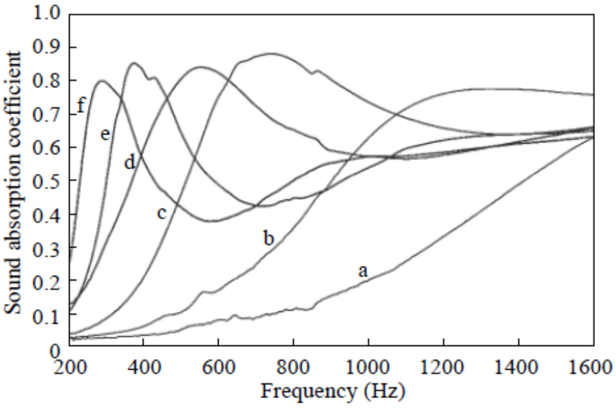

Figure 1. Sound absorption coefficient vs frequency of PVP blankets by increasing mass from *a* to *f*.

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PO-29

Insights into molecular recognition of PD-1/PD-L1 inhibitors

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The programmed death-1 molecule (PD-1) and its ligand (PD-L1) are members of the CD28/B7 superfamily. This protein-protein interaction is involved in regulation of T cells response and in maintenance of peripheral tolerance. Targeting PD-1/PD-L1 interaction can be a promising approach to fight tumors, chronic infections and autoimmune diseases [1]. Bioactive macrocyclic peptidomimetics and small molecules have been reported as PD-L1 binders able to block PD-1/PD-L1 interaction and immune checkpoint functions. At odds with macrocyclic peptidomimetics, it has been demonstrated that small molecules [3] induce PD-L1 dimerization, binding into a shallow cleft of the protein [2]. With the aim of investigating the molecular basis of such interactions, we performed docking studies and molecular dynamic simulations of the two different chemical classes of PD-1/PD-L1 inhibitors. In this communication, results will be presented that allow the identification of critical amino acids accounting for different specificities of small molecule and macrocyclic interactions to PD-L1. While pending for further experimental appraisals, these data provide clues for the rational design of new small molecules as functional peptidomimetics of PD-L1.

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PO-30

Mechanistic insights of hydrolytic activity into a *de novo* functional “Frankenstein” protein framework

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De novo protein design represents an attractive challenge in which both structure and function are built from scratch. Indeed, these enzyme-like catalysts could play a pivotal role for manipulating and obtaining small molecules with prospective applications in medicine and industrial biotechnology [1]. Recently, this goal was achieved with the installation of the esterase activity into an entirely *de novo* designed homo-heptameric peptide assembly (CC-Hept) [2]. The reaction mechanism of CC-Hept, obtained by engineering the functional catalytic triad (Cys-His-Glu) into a channel, is proposed on the basis of a combined molecular dynamics (MD) and hybrid quantum mechanics/molecular mechanics (QM/MM) investigation (**Figure 1**). The preliminary MD simulations have been performed on both unbound and bound to the model substrate (p-nitrophenyl acetate) protein, thus supporting the stability of *de novo* protein architecture. Two reaction pathways have been deeply analyzed at QM/MM level evidencing the rate determining step in agreement with the observed kinetics evidences. The roles of water molecules and of Cys-His-Glu catalytic triad have been highlighted at atomistic level. Our results should be useful for future developments of more selective and efficient engineered enzymes.

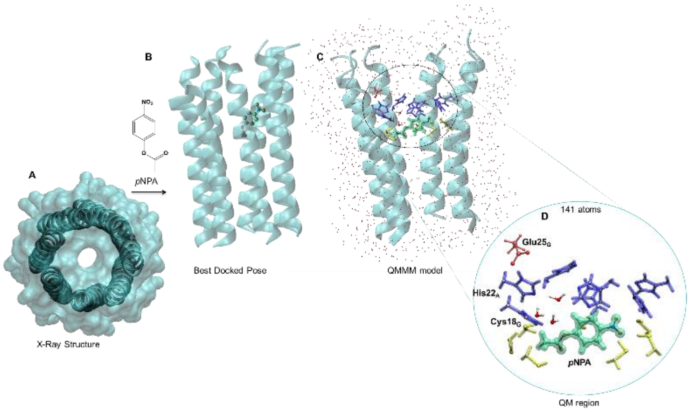

Figure 1. (**A**) Crystal structure of CC-Hept (**B**) *p*NPA-bound protein (**C**) Extrapolated QM/MM model from 100 ns of MDs. (**D**) Focus on QM region residues involved in the proposed catalytic mechanisms.

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PO-31

Thymol derivatives into lignin microcapsules: synthesis, encapsulation and delivery

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An easy, sustainable and low-cost procedure for the synthesis of brominated thymol derivatives has been recently developed in our group. These molecules show important biological activity as antibacterial, antifungal and antiparasitic agents [1,2]. Yet, the poor solubility in water, the pronounced fragrance as well as the high volatility of such compounds often limit their potential application, thus several systems have been recently developed to encapsulate thymol and other essential oils components in order to facilitate their use. Interestingly, it has been found that encapsulated active components preserve their functional properties and their biological activities may be even enhanced. The adoption of an encapsulating material possessing relevant antibacterial and antioxidant activity as well as high biocompatibility, such as lignin, constitutes an ideal strategy for the development of advanced smart materials [3].

In this communication, preliminary results related to the encapsulation of thymol and bromothymol derivatives into lignin-microcapsules will be presented. Moreover, the characterization of the microcapsules and the first studies on the active ingredient delivery will be discussed.

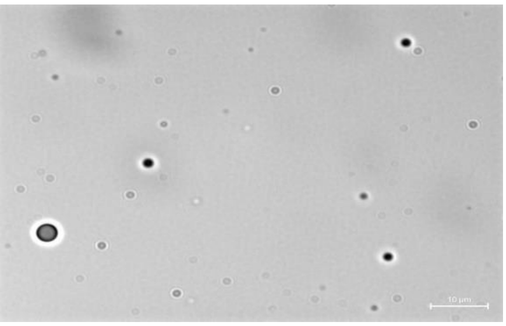

Figure 1. Optical microscopic image of bromothymol-containing Lignin Microcapsules.

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PO-32

An atomistic view of the YiiP structural changes upon zinc(II) binding

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Molecular dynamics can be particularly useful in the study of biosystems hard to treat with experimental techniques, such as proteins embedded in a lipid membrane. In the field of metal transporters, the cation diffusion facilitator family (CDF) is responsible of cations removal from cytoplasm [1]. The human family members, named ZnTs are involved in many severe diseases. However, structural information about ZnT proteins completely lack. The absence is partially compensated with the well-characterized YiiP antiporter from *Escherichia coli* [2]. YiiP is accountable for zinc(II) efflux from the cell; its structural features consist in a transmembrane domain (TMD) connected to a cytoplasmic domain (CTD). The signal from the CTD to the TMD is transmitted through four interlocking salt bridges located at the juncture of the two domains. YiiP is a Y-shaped homodimer with six TM helices for each monomer. Each protein chain carries three zinc(II) binding sites (A-C). Among them, the transport site (site A) is located at the center of the TMD. The low-resolution cryo-EM structure of the YiiP homolog from *Shewanella oneidensis* (PDB 3J1Z) provided a view of the inward-facing state (IF) [3]. This conformation allows the zinc(II) ions to bind the transport site from the cytosol.

We investigated some important aspects of the YiiP zinc(II) transport mechanism performing MD simulations of the model built on the IF state in presence of zinc(II) ions in solution. Our simulations elucidated the zinc(II) interaction pathway from the cytosol to the transport site. The zinc(II) binding to the transport site triggered large-scale conformational changes affecting the channel permeability. Finally, umbrella sampling simulations were carried out to measure the metal-dependent free-energy profiles of zinc(II) and sodium(I) ion going through the channel.

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PO-33

DSSC: a synthetic approach for FRET increasing LHE dyes

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Since the early nineties, dyes have been extensively studied for application in photovoltaic technologies such as dye-sensitized solar cells (DSSC). Large libraries of different kinds of dyes have been synthesized in order to increase solar cell efficiency [1].

Within the last of these families, our group has focused its attention on D-π-A organic molecules. Upon light absorption, this particular structure allows intramolecular charge transfer (ICT) process from donor to acceptor. To have an efficient ICT process molecules must have the HOMO localized over the donor region and the LUMO over the acceptor one [2].

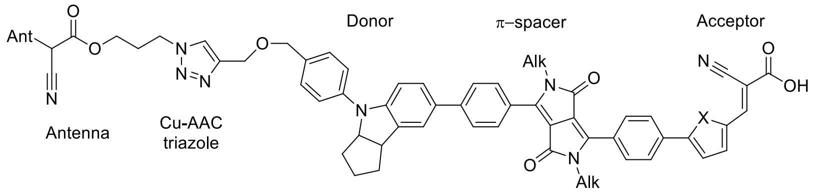

Figure 1. Model of dye-antenna coupled molecule.

Light Harvesting Efficiency (LHE) is one of the critical points for dyes aimed at solar cells application; on the other hand the design and the synthesis of these compounds, with high molar extinction coefficient in a large range of wavelength, can result challenging.

The aim of this work has been to design a photosensitizer able to exploit Forster Resonance Energy Transfer (FRET) [3] to increase the LHE. This can be realized linking a series of fluorescent donors (antennas) to the dye.

To verify this concept we decided to prepare a model dye to be coupled to a series of fluorescents antennas, using the Cu(I) azido-alkyne coupling (CuAAC) click reaction as a simple and versatile synthetic tool. The methodology is very promising as it might allow the preparation of libraries of dyes to measure the LHE values due to FRET effect.

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PO-34

Biomimetic hybrid nanoconstructs for cancer therapy

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In the last few years there has been an increasing interest in nanomedicine and in particular in developing nanoparticles to fight cancer [1].

Zinc oxide nanocrystals (ZnO NCs), thanks to their peculiar properties, can be employed for cancer diagnosis and therapy. Even if the cytotoxicity mechanism of ZnO NCs is not totally understood yet, it is most probably due to the combination of intracellular Zn^{2+} cations release and the production of reactive oxygen species: in vitro tests have also shown an increased cytotoxic effect of ZnO on cancer cells with respect to the healthy counterpart [1].

In order to promote the stability of ZnO NCs in physiological environment, increase their biocompatibility and reduce their immunogenic effects, we covered ZnO NCs with a biomimetic phospholipidic bilayer [2] derived from extracellular vesicles, in particular exosomes, obtaining a nanoconstruct called TrojaNanoHorse (TNH).

Exosomes are naturally produced by many types of cells as vehicle of intercellular communication and, when autologous, they are not recognized by the immune system. We extracted exosomes from living cells and we re-used them as a biomimetic, nature-derived coating to stabilize and reduce the immunogenicity of the ZnO NCs. Most importantly, we would like to exploit the natural communication function of exosome to drive the therapeutic nanoparticles towards the cancer cells [3].

We optimized the coupling process between ZnO NCs and exosomes through a systematic study of the thermodynamic, kinetic and electrostatic parameters of the process and then we tested the efficiency of coupling by combining different characterization techniques.

These experiments on the TNH preparation are the starting points to further study the TNH internalization process, mechanisms of causing cell damages, stability in biological fluids, and targeting mechanisms, to make TNH a new theranostic nanoconstruct against cancer.

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PO-35

Analysis of volatile organic compounds in packaging of mozzarella cheese and yogurt

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Foods come into contact with many materials and articles during its production, processing, storage, preparation and serving, before its eventual consumption. These are called Food Contact Materials (FCMs). Dairy products are usually sold in packaging made of polymeric materials. These are able to release undesirable substances in food, modifying its characteristics and organoleptic properties. In fact, diffusion phenomena can occur [1]. Food Contact Regulations in EU (Regulation (EC) No. 1935/2004 and further reviews) set out general requirements for all FCMs. For plastic food contact materials, EU Commission provides specific measure, that sets out a Union list of authorized substances. Specific migration limits (SML) and restriction conditions for some substances on the positive list and maximum overall migration limits (OML) for the plastic food contact materials (60mg/kg food) were listed. If some substances are not included, the EU Member States set their own national provisions.

This study mainly focuses on determination of organic volatile substances released from plastic material packaging in mozzarella cheese and yogurt, in particular on styrene and isododecane. The analyses were made by P&T-GC-MS with cryogenic trap. Quantitative analysis of styrene and isododecane was performed both at room temperature and at 70 °C. Moreover, qualitative analyses were carried out.

The packaging was made of polyethylene and nylon, and polystyrene for mozzarella cheese and yogurt, respectively. Aromatic, cyclic, linear and branched aliphatic hydrocarbons in the packaging and foods were found. However, isododecane and styrene were the mainly compounds present. Isododecane is probably used as a diluent for the radical initiator for the polymerization while styrene is the polystyrene monomer. The quantitative analysis showed higher amount of isododecane and styrene in the packaging than foods. OML was not exceeded, however, SML for these compounds does not defined in the regulation.

This study highlighted the importance of monitoring the presence of organic volatile compounds since they could be source of human health-related risk during the assumption of the food product.

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PO-36

Occurance of heavy metals in sediments and biota in Northern Adriatic Sea

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Due to the low depth and the modest water exchange, Adriatic Sea is considered a fragile area. In particular, the Northern area receives fresh water input from a series of sources; the most important one is the Po River which drains intensely cultivated and industrialized hinterland areas and releases into the sea great amounts of dissolved and particulate materials, including anthropogenic contaminants.

The aim of this study was to monitor heavy metals concentrations, in biotic and abiotic samples. Heavy metals, especially mercury, are often present in industrial and municipal effluents and are ubiquitary pollutants frequently detected in the environment that can cause long-term effects on marine ecosystems. In particular, samples of sediments, fishes and filter-feeding organisms, collected in the North-Est area of Adriatic Sea were analyzed. The samples were homogenized and digested with nitric acid and hydrogen peroxide by using microwave-oven technique. The analyses were performed by graphite furnace absorption spectrometry (Cd and As), atomic emission spectrometry (ICP-AES) (Ba, Cr, Fe, Mn, Ni, Pb, Cu and Zn) and cold vapour atomic absorption spectrometry after amalgamation traps on gold for the preconcentration of mercury in order to lower the detection limit of the analyte.

Sponsors talks

SP-1	Claudio CARRARA
SP-2	Sara TORTORELLA
SP-3	Massimiliano BEARZOT
SP-4	Carlos RODRIGUEZ DEL RIO
SP-5	Alice SOLDA’
SP-6	Roberta COSTANTINI Federica LA DOGANA
SP-7	Manuela VACATELLO
SP-8	Dario SMACCHIA

SP-1

Water electrolysis: case study of innovation at De Nora

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De Nora (www.denora.com) is the largest worldwide player in industrial electrochemistry. Founded by Ing. Oronzio De Nora in 1923, the company distinguished itself as a top-level supplier of electrodes and plants for chlorine and caustic soda production.

Since the ‘60s, De Nora moved into a series of joint ventures and acquisitions that broadened the presence of the group worldwide, opening to new businesses in electrochemical and water technologies.

Today most part of the electrochemical industry operates electrodes and plants provided by De Nora, that holds the vast majority of the market shares in Chlor/Alkali, surface finishing, plating for electronics, cathodic protection, industrial and pools disinfection, and water and waste water treatment solutions.

More recently, De Nora started playing a key role in the field of hydrogen production by Water Electrolysis (WE).

Thanks to its highly qualified R&D team, divided among four locations in 3 continents, De Nora is able to provide short- and long-term solutions for industrial scale WE, responding to the market requirements for the best performing H_2 and O_2 production system.

In this talk, De Nora’s “Innovation Approach” deployed to face the water electrolysis challenges will be presented, starting from how the Basic Research and Applied R&D groups, supported by the Open Innovation team, work daily on breakthrough and incremental innovations.

SP-2

Chemistry meets society: the new interdivisional group of the Italian Chemical Society

Sara Tortorella,[a,b] Stefano Cinti,[b,c] Elena Lenci[b,d] Adriano Intiso,[b,e] Valeria Costantino,[b,f] and Alberto Zanelli[b,g]

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[b] Gruppo Interdivisionale di Diffusione della Cultura Chimica, Società Chimica Italiana, Viale Liegi 48c, 00198-Roma, Italy
[c] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133-Roma, Italy
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Research communication, dissemination and exploitation are three mandatory activities for researchers applying for grants (e.g., Horizon2020, Marie Skłodowska-Curie Actions) [1].

However, we live in a transition period in which young researchers are asked to prove such new skills indeed, but those skills are poorly transferred during traditional undergraduate and postgraduate courses.

Moreover, such disability in effectively communicating the beauty and the crucial role of Chemistry for the well-being and technological development of our society has undoubtedly contributed to build the dramatic antiscientific scenario we currently face.

To address these issues, the Italian Chemical Society recently established a new interdivisional group focusing on Chemistry dissemination, communication and spreading of a knowledge-based chemical culture.

In this talk, reasons for the creation of such group will be addressed, and main aims and objectives will be also proposed to inspire further discussion. Moreover, a review of the activities proposed by the group, as well as an outline of future activities, will be given.

[1] "Communicating EU research and innovation", European Commission, Horiz. 2020, 2014, 1–13.

SP-3

How to write great papers: from title to references, from submission to publication

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Good research deserves to be published, to be widely read, and to be recognized by your fellow researchers and community. The current research (and funding) climate makes it even absolutely necessary that you are successful in being able to be published: "Publish or Perish". This then raises the question, how can you achieve that goal?

"Success" essentially depends on three components: 1) the ability to determine the best possible publication strategy for your research findings, 2) the best possible way to write your article, and 3) the most effective interaction with editors. Key to success in this context is your ability to put yourself in the position of readers, reviewers and editors.

Key considerations in journal selection are a realistic assessment of the quality of the research and the audience you intend to reach. As an example of the latter: publication in a clinically oriented journal may require more background information on the chemical/pharmaceutical aspects of the research, but more detailed clinical results, whereas the opposite is the case when you publish the same research in a pharmaceutical journal.

The art of manuscript writing is not just applying one "golden tip". It is essentially "telling your story" to your readers in an engaging way, and avoiding common mistakes and deficiencies including poor language. Avoidable mistakes can lead to unnecessary rejection of your manuscript.

Finally, it is your open, non-defensive attitude towards the editors and the reviewer comments, that will not only increase the likelihood of getting your manuscript accepted for publication, it is also likely that your published paper has improved thanks to their comments.

By consistently applying these principles you are likely to become a more successful author.

SP-4

Reaxys: don't reinvent the wheel. Drive it!

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In the last few years the amount of published has dramatically increased.

A way to find the information needed in a faster way is needed to keep project funding in good shape. Reaxys provides rapid and easy access to experimental facts to empower chemistry research, chemical discovery and scientific education. Finding relevant literature, retrieving precise compound properties and reaction data has never been easier. Furthermore, universities require chemistry informatics solutions that address both teaching and research challenges. Since funding is limited, having one solution that covers more tasks is very important.

Reaxys is simple enough to use with undergraduate students in the classroom, but relevant and powerful enough to help researchers prepare for his laboratory work. Reaxys provides a simple and streamlined workflow that can be applied to both education and lab work, saving precious time in both areas.

SP-5

EYCN - the European Young Chemists' Network

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The European Young Chemists' Network (EYCN), the young member's division of EuChemS, is a motivated team of young scientists from 25 different European countries 27 Societies.

The EYCN spent the last years working towards promoting the exchange of knowledge, experience, new ideas and projects among young chemists coming from academia and companies. One of the aims is also to improve the visibility of chemistry, bring it closer to a wider audience and to people from outside the research field - such as industry, business and management. Moreover, the EYCN wants to support young chemists at the beginning of their career with awards and activities focused on developing soft-skills and expanding their possibilities. EYCN sponsors award all around Europe and every two years, we announce the Young Chemist Award (EYCA) in collaboration with SCI and the FNCF. The EYCN organizes career days and has promoted the Young Chemists Crossing Borders exchange program (YCCB) in collaboration with the Younger Chemists Committee of the American Chemical Society (ACS YCC) since 2011 [1].

The EYCN will host the 2nd European Young Chemists' Conference (EYCheM) in Bremen (DE) – registration on https://www.jcf-fruehjahrssymposium.de. Our network offers a mentoring program for Marie Curie fellowship and ERC starting grant applicants: seminars will be soon online on our YouTube Channel. **Keep posted!** If you wish to get in touch with us, please visit our website www.eycn.eu, or contact us using our social media profiles on Facebook (@EYCN), Twitter (@YoungChemists) or LinkedIn.

We look forward to collaborating with you!

Figure 1: EYCN Delegates attending the 13th Delegates Assembly in Torino (ITA).

[1] U.I. Zakai, N. LaFranzo, C. Dunne and J. Breffke, *ChemViews* 2015.

SP-6

Come preparare un buon cv e come affrontare un’intervista di successo

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Il curriculum inviato sarà letto? Si è davvero pronti per affrontare un colloquio di lavoro? I recruiter di Merck mettono a disposizione la loro esperienza per dare consigli pratici su come scrivere un buon curriculum, quali tipi di interviste esistono e come affrontare un colloquio di successo!

SP-7

Bridging the gap from biology to chemical production

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At Merck we collaborate with chemists to make new chemistry available globally. New chemistry that helps accelerate discovery in important fields that improve human life, like for example in drug discovery. Here are introduced some innovative products that are bridging the gap from biology to chemical production. Building blocks that are specifically designed by us for specific use like to develop biological probes and protein degraders. Also a brief introduction of our new software for retrosynthesis Synthia.

SP-8

A possible solution for substitution of substances of very high concern: formaldehyde and perfluoroalkyl substances

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One of VINAVIL S.p.A. (part of MAPEI Group) main goals is to replace in its products all the substances identified by the European Chemicals Agency (ECHA) as SVHCs (substances of very high concern). Currently all the efforts are focused on the substitution of formaldehyde, already within in some of the VINAVIL S.p.A. products, and the perfluoroalkyl substances, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). Formaldehyde and the perfluoroalkyl substances were included by the ECHA in the REACH regulation SVHCs list in 2011 and 2013 respectively [1].

Formaldehyde is identified as carcinogenic substance of category 1B while PFOA is included as toxic for reproduction and persistant, bioaccumulative and toxic (PBT).

First, this work will list the methods of analysis that R&D department of Vinavil uses to determine the concentration of formaldehyde in each life stage of its products, from the storage of raw monomers and other substances, to production stages and in the end to the final use by the customers. Then, will be illustrated the adopted solutions to reduce formaldehyde emissions, changing polymerization initiators, crosslinking monomers and bactericides systems, and to eliminate any residual traces of this hazardous organic molecule using several scavenger combinations. The product Vinavil CRILAT 1815 will be briefly presented as a positive example of how VINAVIL succeed in complete formaldehyde elimination in a product for textile applications.

In the second part it will be shown how VINAVIL S.p.A. is dealing with the issue of the elimination of perfluoroalkyl substances from textile products, especially in the field of high technical facilities (e.g. winter sports clothes). Obtain fabric treatments with high hydrophobic and oleophobic performances using fluorine-free monomer will represent a hard challenge to face.

Details of some chemical reactions together with some examples of process technology modification and the use of selected additives for the reduction of residual traces will be illustrated.

[1] https://echa.europa.eu/it/candidate-list-table.

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Società Chimica Italiana

The Italian Chemical Society (Società Chimica Italiana, SCI), founded in 1909 and erected as a Legal Institution with R.D. n. 480/1926, is a scientific association that includes more than 3400 members. SCI members carry out their activities in universities and research institutes, schools, industries, public and private research and control laboratories, or as freelancers. They are joined not only by the interest in chemical sciences, but also by the desire to contribute to the cultural and economic growth of the national community, improving the quality of human life and the protection of the environment.

For new members

All Merck Young Chemists Symposium participants are (or have just become) SCI members.

Those who, before reaching Rimini, were not yet SCI members will be contacted shortly (by e-mail) to complete the membership procedure and indicate the preferred SCI division.

Those who have chosen to become members for a year will be enrolled until 31/12/2019; those who chose the two-year membership will be SCI members up to the end of 2020.

SCI Giovani / SCI Young

Tutti i soci SCI con meno di 35 anni fanno parte del Gruppo Giovani. Si tratta di un gruppo interdisciplinare che propone svariate iniziative ai suoi membri: il Merck Young Chemists Symposium, i premi Levi e Reaxys, diversi workshop come Y-RICh, CV Clinic Day e Design Your Future, utili alla preparazione di progetti europei per giovani ricercatori, la creazione di network di collaborazione, lo sviluppo di soft-skills individuali, e molto altro ancora.

Società Chimica Italiana
Gruppo Giovani

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