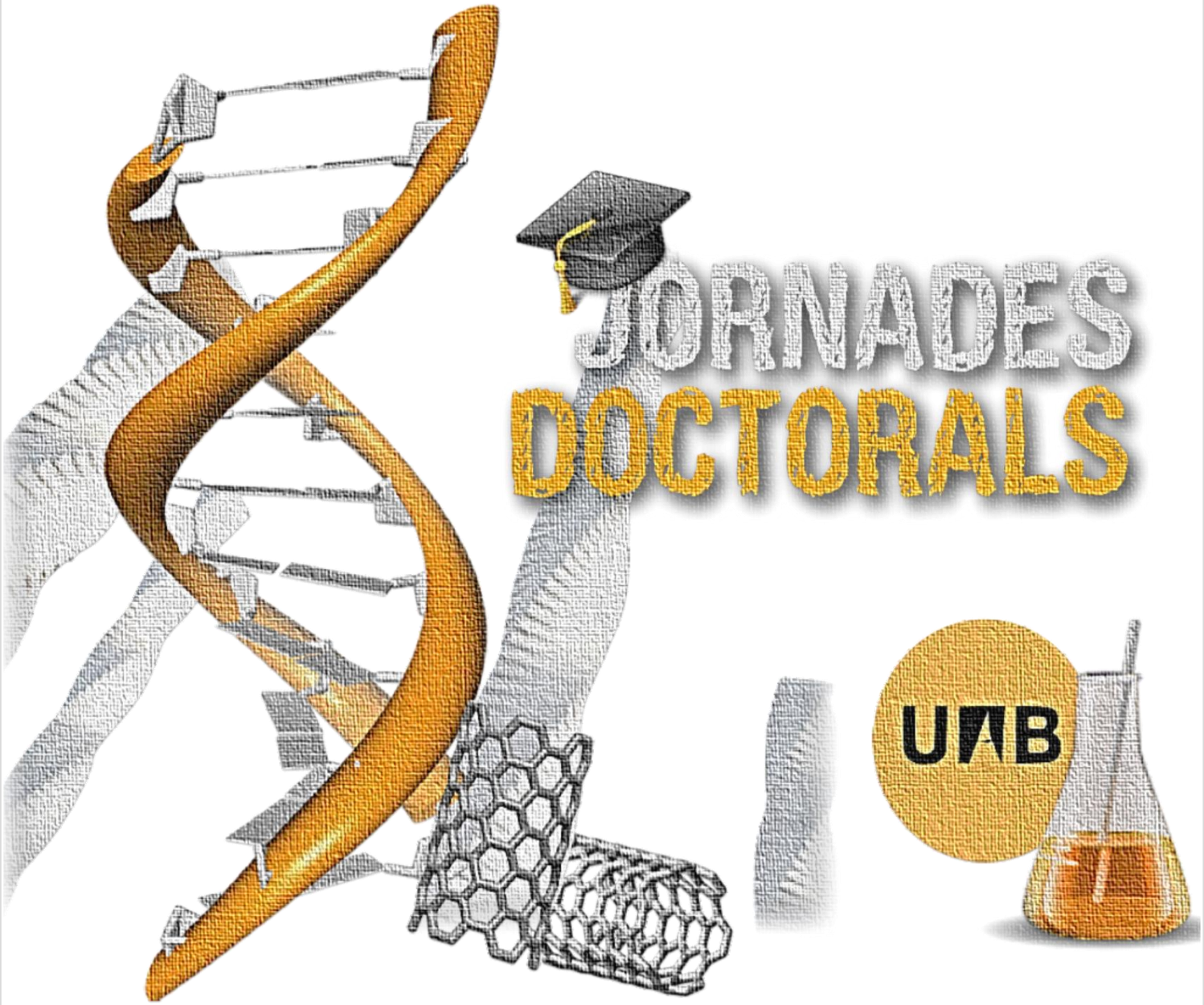

Department of Chemistry

May 30 to June 1, 2018

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WELCOME TO JORNADES DOCTORALS 2018

May 30 – June 1, 2018

It is our great pleasure to welcome you to the "Vuitena Edició de les Jornades Doctorals" that are organized by the PhD Chemistry Program and the Chemistry Department. This event aims to strengthen the links between the research groups of our Department, with the ultimate goal of promoting interdisciplinary and more ambitious research projects. In addition, it aims to relate the chemical research performed by the PhD students of the UAB Chemistry PhD program, and related programs, with Industrial and Entrepreneurial Opportunities. In this eighth edition, the "Jornades Doctorals-2018" includes an exciting series of conferences by 3rd-4th year UAB-Chemistry PhD students and three lectures by academic experts.

Prof. Dr. Christoph Janiak, Full Professor at the Institute for Inorganic Chemistry and Structural Chemistry, University of Düsseldorf

Christoph Janiak obtained his PhD at the Technische Universität Berlin in 1987, followed by postdoctoral stays at Cornell University with Prof. Roald Hoffmann and at BASF AG, Ludwigshafen in the polyolefin division. Since 2010 he is full professor for Bioinorganic Chemistry and Catalysis at the University of Düsseldorf. Dr. Janiak has received several awards such as the Heinz-Maier-Leibnitz award (1991), the ADUC award for habilitands (1996) or the Heisenberg fellowship award (1997). He is serving or has served on the Editorial and Advisory Boards of Crystal Engineering Communications (CrystEngComm, RSC, 2006-2011), Inorganica Chimica Acta (Elsevier, 2013-2016), Nano Structure & Nano Objects (2014-2016), ChemistryOpen (Wiley, from 2012) and Zeitschrift für Anorganische Allgemeine Chemie (Wiley, since 2009). His main research interests are porous coordination polymers/metal-organic frameworks, metal nanoparticles also in ionic liquids, catalysis and supramolecular structural chemistry. He is co-author of about 420 journal publications, book chapters, text books and patents.

+ information: http://www.janiak.hhu.de/

Prof. Dr. Guillem Aromi, Aggregate Professor, Department of Inorganic and Organic Chemistry, Universitat de Barcelona. Director of the Institute of Nanoscience and Nanotechnology (IN2UB)

Dr. Guillem Aromí graduated in Chemistry and Chemical Engineering at the University of Barcelona (UB) and EHICS (Strasbourg, France), respectively. He earned his PhD in Chemistry at Indiana University (USA) in 1999 and completed posdoctoral stays at Leiden University (Holland) with a Marie Curie Fellowship and at Manchester University (UK). He became in 2003 a "Ramon y Cajal" Fellow at the UB where he is Aggregate Professor of Chemistry since 2007. Dr. Aromí was awarded the UB/Generalitat de Catalunya distinction for "enhanced research profile" and an ICREA Academia twice, in 2008 and 2013. He is also recipient of an ERC Starting Grant. His research interests focus on the design, synthesis and study of molecular functional materials, as a way to face the challenges of Nanotechnology, with three main lines: a) design and preparation of molecules for Quantum Computing (QC) through the coherent manipulation of spins, b) preparation and study of switchable materials based on spin crossover (SCO), and c) preparation of magnetic photoswitchable molecules. He is coauthor of about 180 papers.

+ information: https://www.gmmf-ub.com/who_we_are

Dra. Silvia Osuna Oliveras, ICREA Researcher Professor, Universitat de Girona

Sílvia Osuna received her PhD in 2010 from the University of Girona (UdG) at the Institut de Química Computacional (IQC) under the supervision of Prof. Miquel Solà and Prof. Marcel Swart. In 2010, she moved to the group of Prof. Houk at the University of California, Los Angeles (UCLA) thanks to the IOF Marie Curie fellowship. Since then, Sílvia has worked in computational design of enzymes of medical and pharmaceutical interest. She currently holds an ICREA research position at the Institute of Computational Chemistry and Catalysis (IQCC) at the University of Girona. Sílvia has more than 60 research publications (h-index = 24), and has been recently awarded the Young Researcher award by the Royal Spanish Society of Chemistry (RSEQ 20116), the Research award by the Fundación Princesa de Girona (FPdGi 2016- Science category), and the 2017 Young Investigator Award of EuCheMS Organic Division. Her group works in the computational design of enzymes of medical and pharmaceutical interest, and is funded as ERC - Starting Grant.

+ information: http://iqcc.udg.edu/wordpress/portfolio/silvia-osuna/

We look forward to your participation in this event.

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- Prof. Mariona Sodupe, PhD Coordinator of the studies in Chemistry and President of the Chemistry PhD Committee (UAB)
- Prof. Félix Busqué, Master Coordinator of the studies in Chemistry and President of the Chemistry Master Committee (UAB)
- Prof. Xavier Sala, Secretary of PhD and Master Studies Committee (UAB)
- Prof. Rosa Mª Sebastian, Vocal of PhD and Master Studies Committee (UAB)
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SCIENTIFIC PROGRAM

May 30

10:00 - 10:15 Opening Ceremony

10:15 - 11:15 Jornades Doctorals Lecture

Chairman: Prof. Daniel Maspoch

"MOFs for water sorption for cycling heat transformation processes"

Prof. Dr. Christoph Janiak

11:15 - 12:00 Coffee Break and Poster Session

12:00 - 13:00 Flash Presentations I

Chairman: Prof. Daniel Maspoch

12:00 - 12:15 Alternative Materials for Bio-sensing: Silk fibroin from *Bombyx mori*. **Augusto Márquez Maqueda** (FP1.1)

12:15 - 12:30 Synthesis of Metal-Organic Frameworks in Supercritical CO_2. **Núria Portolés Gil** (FP1.2)

12:30 - 12:45 Novel Carborane-based Linkers for MOFs: Introduction of Flexibility and Reversible Single-Crystal Phase Transitions. **Fangchang Tan** (FP1.3)

12:45 - 13:00 Study of the regioselectivity of Prostaglandin G2 from Arachidonic Acid catalyzed by Cyclooxygenase-2: A Molecular Dynamics/QM/MM approach. **Anna Cebrián Prats** (FP1.4)

13:00 - 16:00 Break

16:00 - 17:30 Flash Presentations II

Chairwoman: Prof. Rosa Mª Sebastian

16:00 - 16:15 Biomimetic core-canopy quantum dots: ions trapped in voids induce kinetic fluorescence switching. **Arpita Saha** (FP2.1)

16:15 - 16:30 INP@MOF Nanocomposites as NIR-Activated Drug Delivery Systems. **Gerard Boix i Soler** (FP2.2)

16:30 - 16:45 Metallacarboranes, a new electron acceptor generation. **Ana Begoña Buades Martín** (FP2.3)

16:45 - 17:00 Single-Crystal-to-Single-Crystal Solid-Gas Phase Postsynthetic Modification of Metal–Organic Frameworks via Ozonolysis. **Jorge Albalad Alcalá** (FP2.4)

17:00 - 17:15 HspX protein tuberculosis biomarker evaluated in sputum samples by plasmonic biosensing. **Enelia Cristina Peláez Gutiérrez** (FP2.5)

17:15 - 17:30 Development and optimization of a novel tooth whitening treatment. **Clara Babot Marquillas** (FP2.6)

May 31

10:00 - 11:00 Jornades Doctorals Lecture

Chairwoman: Prof. Mariona Sodupe

"Conformational heterogeneity in the evolution of enzyme function"

Dra. Silvia Osuna Oliveras

11:00 - 11:45 Coffee Break and Poster Session

11:45 - 13:00 Flash Presentations III

Chairwoman: Prof. Mariona Sodupe

11:45 - 12:00	Rapid method for the detection of exosomes as a novel biomarker for cancer diagnosis. **Silio Lima de Moura** (FP3.1)
12:00 - 12:15	Sulfonated, trifluoromethylated and carboxylated triarylphosphines. Application in biphasic hydroformylation. **María de las Mercedes Cordón Acedo** (FP3.2)
12:15 - 12:30	NIRS and Chemometrics applied to challenging conditions in pharmaceutics, forensics and biotechnology. **Aira Yira Miró Vera** (FP3.3)
12:30 - 12:45	Optimised azobenzene photoswitches for reliable two-photon neuronal excitation. **Gisela Cabré Segura** (FP3.4)
12:45 - 13:00	Designing water-soluble sulfonate and arginine-rich bioconjugated Cu(II) complexes with anticancer properties. A redox-active metallic core. **Joaquim Peña Aparicio** (FP3.5)

13:00 - 16:00 Break

16:00 - 17:30 Flash Presentations IV

Chairwoman: Prof. Clara Viñas

16:00 - 16:15	From Surface to Nanoparticles: Ruthenium Oxide (RuO_2) Systems and Their Interaction with Water. **Javier Heras Domingo** (FP4.1)
16:15 - 16:30	Potential radiopharmaceuticals: "from synthesis to pre-clinical trials". **Jordi Borras Amoraga** (FP4.2)
16:30 - 16:45	Amperometric rGO-Nanocompostives Electrochemical Sensors Functionalized With Metal Nanoparticles. **Jordi Rodríguez Rodríguez** (FP4.3)
16:45 - 17:00	Optimisation Studies of Hard Carbon Negative Electrodes for Sodium Ion Batteries. **Enrique Irisarri Jiménez** (FP4.4)
17:00 - 17:15	Applications of the cyclobutane scaffold in new cell penetrating agents for drug delivery. **Jose Antonio Olivares Montia** (FP4.5)
17:15 - 17:30	Chemoselective polymerization using difunctional monomers: Towards polyacrylates with pendant cyanoacrylate moieties. **Cristina Monfort Fraga** (FP4.6)

June 1

10:00 - 11:00 Flash Presentations V

Chairman: Prof. Xavier Sala

10:00 - 10:15 The mechanism and adsorption study of Pine biomass and pyrolyzed Pine loaded with TiO_2 in aqueous solution. **Jingjing Zhao** (FP5.1)

10:15 - 10:30 A novel potentiometric microsensor for real-time detection of Irgarol using the ion-pair complex [Irgarol-H]+[$Co(C_2B_9H_{11})_2$]. **Abhishek Saini** (FP5.2)

10:30 - 10:45 Printing technologies for biotechnological and environmental sensing applications. **Roberto Pol Arcas** (FP5.3)

10:45 - 11:00 Glycine polymerization catalyzed by the TiO_2 (101) anatase surface. **Stefano Pantaleone** (FP5.4)

11:00 - 11:45 Coffee Break

11:45 - 12:45 Jornades Doctorals Lecture

Chairman: Prof. Xavier Sala

"Solid State Transformations: A Gate to Polymorphism or Multi-stability in SCO Coordination Complexes"

Prof. Guillem Aromi

12.45 - 13:15 Award and closing ceremony. Jornades Doctorals 2018 distinguished Diploma, along with a gift, will be given to the three best Poster-Flash Presentations (Gifts: IPad for the 1st place, Bluetooth speaker for the second place and Wireless Headphones for the 3rd place). **Prizes awarded by HNA Group**

JORNADES DOCTORALS 2018

LECTURES

MOFs for water sorption for cycling heat transformation processes

Christoph Janiak

Institut für Anorganische Chemie und Strukturchemie , Heinrich-Heine-Universität Düsseldorf, 40204 Düsseldorf, Germany. Email: janiak@uni-duesseldorf.de

Metal-organic frameworks (MOFs) with water stability and high water uptake capacity are gaining attention for reversible cycling water sorption in order to achieve low temperature heat transformation applications in thermally driven adsorption chillers (TDCs) or adsorption heat pumps (AHPs) (Fig. 1). Sorption chillers or heat pumps are an alternative to conventional compression systems operating with high input of electricity, largley generated from fossil fuels. By using low grade heat as the driving energy, TDCs or AHPs can significantly help to minimize primary energy consumption and greenhouse gas emissions generated by industrial or domestic heating and cooling processes. TDCs and AHPs are based on the evaporation and consecutive adsorption of coolant liquids, preferably water. The process is driven and controlled by the microporosity and hydrophilicity of the employed sorption material. We present current basic research developments and critically discuss the potential of MOFs in adsorption chilling or adsorption heat pump processes (Fig. 1).[1,2]

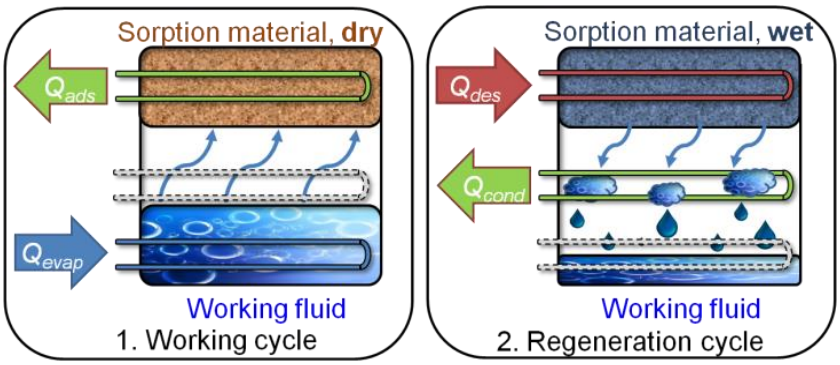

Fig. 1 Principle of adsorption chilling or adsorption heat pump.
Working cycle: A working fluid (typically H_2O) is evaporated at low pressure by application of evaporation heat Q_{evap}, and adsorbed at a microporous material, releasing adsorption heat Q_{ads}.
2. Regeneration cycle: When the adsorbent is saturated, driving heat Q_{des} is applied for desorption of the working fluid. The vapour then condenses in a cooler, and condensation heat Q_{des} is released.

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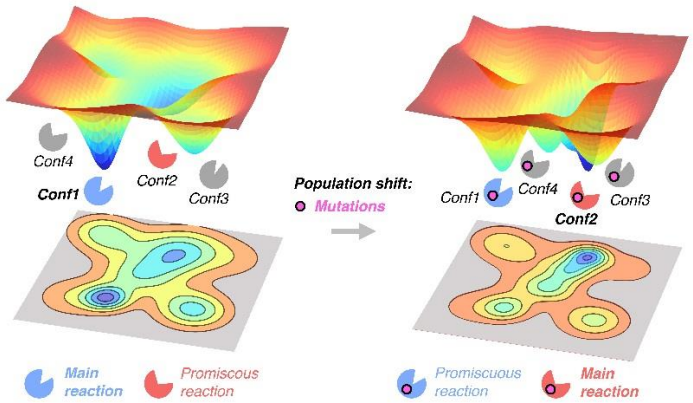
Conformational heterogeneity in the evolution of enzyme function

Sílvia Osuna[1,2], Christian Curado, Eila Serrano-Hervás, Guillem Casadevall, Adrian Romero-Rivera, Marc Garcia-Borràs, Ferran Feixas

[1]Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Carrer Maria Aurèlia Capmany 69, 17003 Girona.

[2]ICREA, Passeig Lluís Companys, 23, 08010 Barcelona.

Enzymes exist as an ensemble of conformations important for their function. By introducing mutations to the enzyme sequence, the populations of the different conformational states can be gradually tuned for allowing novel function. In this talk, the population shift induced by distal and active site mutations introduced along a series of laboratory-evolved enzymes[1-4] is presented. Microsecond time-scale Molecular Dynamics (MD) simulations in combination with correlation-based analysis, Markov State Models (MSM), and enhanced sampling techniques are applied to elucidate the changes in the conformational landscape of laboratory evolved variants. Dramatic changes in the conformational dynamics of active site loops involved in substrate entrance and product release are revealed, which provide a rationalization for the enhancement in catalytic activity of the new evolved variants.[4] Most importantly, our new tools based on inter-residue correlations observed along the microsecond-scale MD simulations provides a strategy to identify the amino acid positions that influence the dynamic properties of laboratory-evolved enzymes.[1] Our method is therefore able to rationalize, but most importantly to predict which residues situated far away from the active site can have a large impact on the enzyme catalytic activity.[1]



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(2) Romero-Rivera, A.; Garcia-Borràs, M.; Osuna, S. *Chem. Commun.* 2017, *53*, 284.
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Solid State Transformations: A Gate to Polymorphism or Multi-stability in SCO Coordination Complexes

G. Aromí,[a]* R. Diego,[a] J. S. Costa,[a] G. A. Craig,[a] C. Bartual,[a] O. Roubeau,[b] C. Beavers[c]

[a]Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, [b]Advanced Light Source, Berkeley Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA, [c]Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC and Universidad de Zaragoza, Plaza San Francisco s/n, 50009, Zaragoza, Spain.
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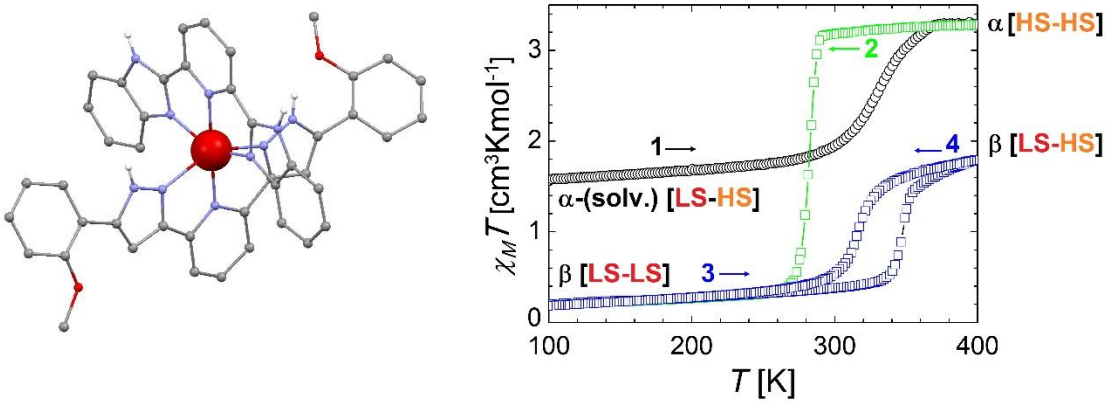
Spin Crossover (SCO) coordination complexes are a rich source of molecular switchable materials for potential spintronic applications. In the solid state, the SCO often couples with crystallographic transitions and/or changes to the composition of the crystal lattice. When such transformations occur in a single-crystal-to-single-crystal (SCSC) manner, X-ray diffraction constitutes a valuable window of information to exploit these solid-state reactions. This rarely happens with materials made of discrete molecules, where the intermolecular interactions may not suffice to preserve the integrity of the single crystals. We have developed a series of Fe(II) SCO complexes with crystal lattices flexible enough to allow a great variety of solid state transformations, while sufficiently robust to maintain single crystal integrity.[1] Some of these compounds have unveiled unique features of solid-state transformations coupled to SCO processes. These include, i) the formation of intermediate phases within a single crystal during the reaction,[2] solid-state pathways to reach polymorphs of SCO compounds,[3] a succession of irreversible phase transitions delineating four different thermal pathways providing four possible magnetic responses, depending on the thermal history of the sample (Figure).



1 G. Aromí, J. S. Costa, G. Craig, O. Roubeau, *et al. J. Am. Chem. Soc.*, **2014.** *136*, 3869.
2 G. Aromí, C. Beavers, J. S. Costa, G. Craig, O. Roubeau, *et al.Chem. Sci*., **2016**, *7*, 2907
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JORNADES DOCTORALS 2018

ABSTRACTS

Alternative Materials for Bio-sensing: Silk fibroin from *Bombyx mori*

Augusto Márquez[1], Gonzalo Guirado[2], Carlos Domínguez[1], Xavier Muñoz-Berbel[1]

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[2] *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*

The field of commercial point of care (POC) tests for glucose monitoring in blood is widely covered with the glucose test strips for electrochemical measuring. Colorimetric analysis in this case is poor developed, while in other preliminary tests (pH, pregnancy, lead acetate) is commonly used. This aspect is logic as blood has a strong red color due to the presence of hemoglobin, what suppose an important interference. To prevent this drawback, cellulose is commonly employed to filter the sample, but also to manage the fluidics and retain the interactive elements (i.e. lateral flow tests).

In this talk, I will present silk fibroin[1] as an alternative to cellulose. This material covers in great part paper functionalities like capillary pumping and filtering but also and present others: i) mechanical properties: possibility to develop thin film biosensors resistant to mechanical stress, ii) biocompatibility: possibility to encapsulate biomolecules without disturbing their activity and also to be implanted in patients, iii) enzyme activity sustainer: the crystalline structure may isolate the immobilized biomolecules from harmful agents, iv) waveguide: besides acting as a biocompatible matrix, the silk fibroin can guide the light in a biosensor, being transparent in the visible and iv) compatibility with micro and nanofabrication technology (stamping, e-beam).

Among the molecules that can be included in the silk fibroin matrix, photoelectrochromic diacid dithienylethene dye[2] is promising since it has demonstrated to be a valid substrate for the horseradish peroxidase and, therefore, compatible with the oxidase-peroxidase detection cycle, in which analytes like glucose, lactate, cholesterol, glycerol, etc… may be detected. The possibility of recover the molecule to the initial state previous to the detection enable the fabrication of a regenerable optic biosensor.

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Synthesis of Metal-Organic Frameworks in Supercritical CO_2

Núria Portolés-Gil [a,b], Ana M. López-Periago [a], Concha Domingo [a] and José A. Ayllón[b]

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[b] *Departamento de Química (UAB), Spain.*
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Clean fluid technologies have become an important field of research in the last years due to the need of developing new materials in a sustainable way, i.e., avoiding the use of toxic organic solvents. Research in metal-organic frameworks (MOFs) has also increased considerably in the last decade, since these materials are potential candidates for numerous applications, such as drug delivery, catalyst, gas separations, gas storage and others [1]. The main aim of this work is to crystalize MOFs using supercritical carbon dioxide ($scCO_2$) as a green solvent. To date, published reports on the use of this solvent in the field of MOFs processing is scarce. The use of $scCO_2$ has normally been applied for the activation or cleaning of these materials [2].

In this work, for MOF synthesis we have chosen reagents that were either soluble or are partially soluble in $scCO_2$, although examples with low solubility were also used. The use of different organic linkers (mainly bipyridine derivatives) allows the design of different porous structures. In the cases where the low soluble building blocks were used, two different approaches were studied: 1) use 5 wt% of ethanol as a co-cosolvent, 2) add *tert*-butyl to modify (in situ or ex-situ) the solubility of the metal complexes. Results showed that the crystallization of several 3D, 2D and 1D MOFs was thus possible. Known and new products could be crystallized following this route. In this presentation three examples are shown: a 3D structure with a stoichiometry of $[Zn(CCM)(H_2O)_{1.5\text{-}2}]_n$ (CCM = curcumin) [3], 2D MOF of $[Cu(tfa)_2(bpp)_2]_n$ (tfa = trifluoroacetate and bpp = 1,4-bis(pyridin-4-ylmethyl)benzene))[4] and 1D MOF of the type of $[M(DeOx)_2(bipy)]_n$ (DeOx = diethyl oxaloacetate, M = Cu, Ni and Mn and bipy = 4,4'dipyridyl)[5]. The obtained compounds were characterized by X-ray diffraction, elemental analysis, and N_2 adsorption for textural properties. Differences in crystal size and morphology were observed by scanning electron microscopy.

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Novel Carborane-based Linkers for MOFs: Introduction of Flexibility and Reversible Single-Crystal Phase Transitions

Fangchang Tan,[1] Ana López-Periago,[1] Mark E. Light,[2] Jordi Cirera,[3] Eliseo Ruiz,[3] Alejandro Borrás,[1] Francesc Teixidor,[1] Clara Viñas,[1] Concha Domingo,[1] Jose Giner Planas[1]

[1] *Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Bellaterra, Spain.*
[2] *Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK.*
[3]*Departament de Química Inorgànica i Orgànica and Institut de Recerca de Química Teòrica i Computacional, Universitat de Barcelona, Spain.*

Keywords: Carborane, Metal-Organic Frameworks, Flexibility

Metal-organic frameworks are constructed by metallic nodes interconnected by a variety of organic linkers possessing regular and porous structures. Carboranes are highly stable spherical molecules with hydrophobic character and showing 3D aromaticity [1]. In this PhD work, we are exploring the use of carborane-based ($C_2B_{10}H_{12}$ clusters) dipyridine ligands in combination with conventional dicarboxylic ligands to build a series of new MOFs. We are currently studying the effect that our carborane ligands have on the properties of the new MOFs. We have recently reported the synthesis and characterization of a novel family of MOFs containing carboranylalcohol ligands and different di-, tri-, and tetratopic carboxylic acids and metal salts [2]. In this work we will concentrate in the flexibility behaviour of one of these MOFs (**1** in Fig. 1).

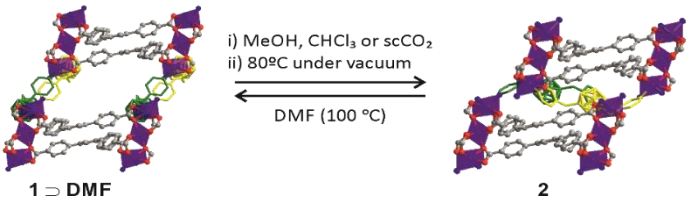

Fig. 1. Optimized conditions for the bulk reversible **1**

MOF **1** behaves as a crystalline sponge for a variety of guests and shows a high affinity for aromatic solvents as guests. Single-crystal nanoindentation experiments indicate that a high number of specific interactions between the aromatic guests and the MOF framework contribute to the stability of **1** [2]. In the absence of such host-guest interactions, an unprecedented solid phase transition can be induced in **1** to generate **2** without loss of the carborane linkers (Fig. 1) [3]. Most interestingly, such transformation is reversible. We will discuss the details for such transformation and how can we take advantage of this process for encapsulating C60.

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Study of the regioselectivity of Prostaglandin G2 from Arachidonic Acid catalyzed by Cyclooxygenase-2: A Molecular Dynamics/QM/MM approach

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Cyclooxygenases (COXs) are heme-containing bi-functional homodimeric enzymes. These enzymes catalyze the prostaglandin (PG) biosynthesis by the addition of two molecules of oxygen to Arachidonic Acid (AA) forming the hydroperoxy endoperoxide PGG_2, that is reduced to PGH_2, a precursor of different prostaglandins and thromboxanes. Three isoforms of COXs exist: COX-1 (a constitutive enzyme), COX-2 (the expression of the enzyme is induced during inflammatory states) and COX-3.

In this work, we have explored the conformational landscape of AA:COX-2 Michaelis complex by means of 100 ns classical Molecular Dynamics (MD) simulation. Subsequently, some MD snapshots were selected to calculate the potential energy surface by a QM(DFT)/MM approach, in order to study all the steps of the catalytic mechanism. The reaction mechanism that transforms AA into PGG_2 is constituted by six steps: the abstraction of the 13-pro*S* hydrogen from AA by the Tyr385 radical; the addition of oxygen (O_2) at C_{11} in an antarafacial way; two cyclizations: the first one at C_9 pro-*R* position with a radical oxygen, and the second one between the $C_8 - C_{12}$ atoms of AA; the addition of another oxygen at C_{15} pro-*S* position and the back hydrogen transfer from Tyr385, to finally yield PGG_2.

The main goal of this project is to analyze the rearrangement of the AA inside the active site of COX-2 and determine how the regioselectivity of the substrate is controlled along the catalytic mechanism to obtain the PGG_2. Understanding in detail the transformation of the AA using a QM/MM approach can be useful to design new selective inhibitors that might control inflammatory activity.

Biomimetic core-canopy quantum dots: ions trapped in voids induce kinetic fluorescence switching

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Closely packed hollow spheres connected through pillars to a CdSe quantum dot (QD) core produce channels through which ions navigate. This particular structure is well represented by [CdSe@CarbOPH(O)]@Cl/[N(Caprylyl)$_3$Me$_1$][1] indicating that in the channels between the canopy made by the carboranyl spheres (carboranylphosphinate, CarbOPH(O)) and the CdSe core exist chloride anions. Due to the close packing, the spheres produce openings. These are converted into gates because [N(Caprylyl)$_3$Me$_1$]+ acts as a plug. If these spheres are placed in a close packing, they generate openings through which ions or solvent molecules can move and cannot be liberated easily, resembling cell membrane transport. The [CdSe@CarbOPH(O)]@Cl/ assembly is negatively charged because the Cd positive charges are outnumbered by the negative charges due to the Se, the phosphinic acid and, very importantly, the trapped chloride anions, and this negative load is compensated by the cationic surfactant.

It is shown in this work that this synergism produces an unprecedented phenomenon, namely, kinetic fluorescence switching. It is observed that the material shines brightly then loses its brightness and, upon the application of kinetic energy, shines back to the maximum power. This process continues for an extended period of time, up to half a year, at least. This new type of architecture in QDs is named as core–canopy QDs. In this case, this study demonstrates one property, the kinetic fluorescence switching, as a consequence of the trapping of Cl− in the QDs channels, but other properties can be envisaged with the judicious choice of the anions or even the pillar connecting the hollow sphere with the ground.

Figure 1. The architecture of [CdSe@CarbOPH(O)]@Cl/[N(Caprylyl)$_3$Me$_1$]

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INP@MOF Nanocomposites as NIR-Activated Drug Delivery Systems

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Metal-Organic Frameworks (MOFs) are hybrid crystalline materials formed by the coordination of a transition metal ion or cluster and a polydentate organic linker. Because of their exceptional porosity and highly tailored structure and composition, MOFs at the nanometric scale have emerged as promising materials for biomedical applications. Noteworthy series of MOFs have recently been reported, exhibiting a wide variety of topologies and compositions, high adsorption capacity, adequate biocompatibility and biodegradation. However, one of the current challenges on using MOFs as platforms for drug delivery is to control the release of the adsorbed drugs. In this communication, we show the design and synthesis of a new class of triggered drug delivery systems based on MOF@Drug@INPs composites (Figure 1). In this platform MOF provide a porous structure with good affinity for the chosen drug to store and safely transport it within the patient's body without accidental release in healthy tissues. The inorganic nanoparticles (INPs) are used to provide a triggered release functionality to the composite; they act as an antenna to absorb Near InfraRed (NIR) radiation and transform it into heat through photothermal effect thereby inducing an accelerated release of the adsorbed drug.

In this work we have synthetized this multifunctional composites using the MOF UIO-66 and gold hollow cages. By impregnating the activated composite with a saturated solution of doxorubicin we can load the drug into the composite with notable success (100% of the composite weight) and monitor its release through fluorescence spectroscopy. A release study has been carried out measuring the desorbed drug concentration over time with and without NIR laser-induced triggered activation.

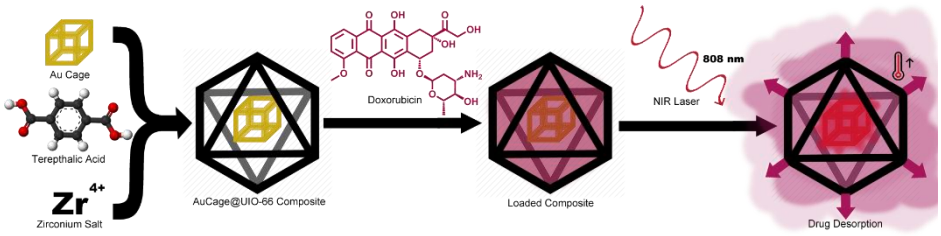

Figure 1: Schematic representation of the MOF@Drug@INPs composite synthesis and triggered release

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Metallacarboranes, a new electron acceptor generation

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With the goal to produce molecules with high electron accepting capacity and low reorganization energy upon gaining one or more electrons, a synthesis procedure leading to the formation of a B-N(aromatic) bond in a cluster has been developed. The research was focused on the development of a molecular structure able to accept and release a specific number of electrons without decomposing or change in their structural arrangements. The synthetic procedure consists of a parallel decomposition reaction to generate a reactive electrophile and a synthesis reaction to generate the B-N(aromatic) bond. This procedure has paved the way to produce the metallacarboranylviologen [M(C_2B9H_{11})($C_2B_9H_{10}$)-NC_5H_4-C_5H_4N-M'($C_2B_9H_{11}$)($C_2B_9H_{10}$)] (M=M'=Co, Fe and M= Co and M'=Fe) and semi(metallacarboranyl)viologen [3,3'–M(8-(NC_5H_4-C_5H_4N–1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)] (M=Co, Fe) electron cumulative molecules. These molecules are able to accept up to five electrons and to donate one in single electron steps at accessible potentials and in a reversible way. By targeted synthesis and corresponding electrochemical tests each Electron Transfer (ET) step has been assigned to specific fragments of the molecules. The molecules have been carefully characterized and the electronic communication between both metal centers (when this situation applies) has been definitely observed through the co-planarity of both pyridine fragments. The structural characteristics of these molecules imply a low reorganization energy that is a necessary requirement for low energy ET processes. This makes them electronically comparable to fullerenes, but on their side they have a wide range of possible solvents. The ET from one molecule to another has been clearly demonstrated as well as their self-organizing capacity. We consider that these molecules thanks to their easy synthesis, ET, self-organizing capacity, wide range of solubility and easy processability can find important application in any area where ET is paramount[1].

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Single-Crystal-to-Single-Crystal Solid-Gas Phase Postsynthetic Modification of Metal–Organic Frameworks via Ozonolysis

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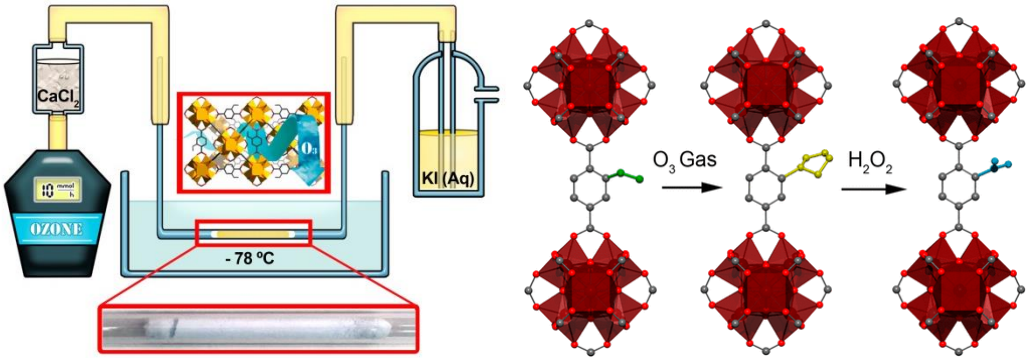
Metal–organic frameworks (MOFs) are crystalline materials that comprise organic linkers and metal ions/clusters. For the past two decades, they have attracted attention for their exceptional properties. Beyond their inherent crystallinity and porosity, MOFs are an ideal platform for applications that entail incorporation of target chemical functionalities onto their pore walls.[1] However, the synthetic conditions of postsynthetic covalent modifications typically require soaking the MOF in a saturated solution of the reagent at high temperatures during long reaction times, achieving at best moderate conversion rates.

By exploring new MOF – gas interactions other than physisorption, we demonstrate that fast and quantitative post-synthetic functionalizations are achievable in solventless conditions. We demonstrate that, by constantly streaming an ozone flux through the MOF for 30 minutes, the pendant alkene groups found in the pore walls can be quantitatively transformed into stabilized 1,2,4-trioxolane moieties on the pore walls, with no loss of single-crystallinity.[2] These trioxolane moieties could be further converted into either aldehyde or carboxylic groups by selective working-up conditions without affecting the framework integrity.

In addition, when the reactive olefin group is integrated inside the organic backbone of the MOF, we can selectively etch the framework, inducing mesoporosity and bigger pore windows.



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HspX protein tuberculosis biomarker evaluated in sputum samples by plasmonic biosensing

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Tuberculosis is a disease that has caused the higher rate of morbidity and mortality worldwide. The World Health Organization estimates that there are 10.4 million new cases and 1.7 million deaths each year, mainly occurring in developing countries. Advances in detection and diagnosis techniques and the introduction of new therapies have substantially increased patient survival rates over the past few years. However, there are limitations related to the inefficiency of real time detection: techniques and laboratory methods have low specificity which leads to misdiagnosis, instruments are still expensive and highly trained staff is still needed. To contribute to the detection of tuberculosis, the HspX protein has been used as a biomarker. It is a 16 kDa protein known as α-crystallin homologous protein (encoded by the gene *hspx* 435 bp). It was originally described as a dominant antigen of *M. tuberculosis* observed in serum and sputum of patients. Some studies suggest that HspX protein plays an important role in the pathogenesis of tuberculosis, as it is required for the growth of *M. tuberculosis* in human macrophages cultures and reduces the inactivated gene expression. Due to its high immunogenicity, the HspX protein has been used in the development of new diagnostic tests or in the construction of new vaccines. The use of this biomarker for biosensing strategies could offer a valuable alternative for diagnosis of tuberculosis for early detection and rapid quantification.

In the present study, we have obtained HspX recombinant protein using molecular biology techniques to its expression and purification. Subsequently, a label free Surface Plasmon Resonance (SPR) based direct immunoassays was developed for the detection and quantification of this protein in sputum samples, without the need of using any marker or amplification step. The plasmonic sensor was modified with a mix of thiolated self-assembled monolayer (SAM) containing carboxylic groups to further allow a direct and rapid quantification of HspX protein using highly specific monoclonal antibodies. Thiolated groups incorporating ethylenglycol components were used to reduce non-specific adsorptions of samples. Results show a Limit of Detection (LOD) of 49.6 ± 2.1 pM (794 ± 0.03 pg/mL) and a Limit of Quantification (LOQ) of 167.1 ± 7.0 pM (2.67 ± 0.1 ng/mL). The potential of measuring directly in pre-treated sputum of tuberculosis patients has also been demonstrated with high reliability in concentrations of HspX protein among 8 – 20 nM.

Keywords: HspX recombinant protein; protein biomarker; *Mycobacterium tuberculosis*; SPR Immunosensor; Self-assembled monolayer; Point-of-care device; Clinical diagnosis; sputum samples

Development and optimization of a novel tooth whitening treatment

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The demand for tooth whitening has grown exponentially in the last 20 years, being nowadays one of the most popular cosmetic procedure at dentist office and moving millions of dollars per year [1]. Based on hydrogen peroxide or carbamide peroxide at different concentrations (from 0,1 to 35%) [2], whitening treatments perform its action by oxidizing the coloured aromatic molecules adsorbed into the teeth enamel (e.g. tannins contained in coffee, tea or wine) making them colourless [3]. Normally, whitening treatments require long application times (over two to four weeks, for 30 minutes to one hour at a time) [4], that can lead to side effects such hypersensitivity, sore throat or white patches on the gum line [5]. A faster, more efficient, user friendly and safer bleaching technique could be of interest both for users and manufacturers. The main aim of this work was to find a new whitening agent, with faster and greater bleaching effects than the commercial treatments (based on carbamide peroxide), as well as to try to reduce the secondary effects. To accomplish with the first objective (novelty), we explored a different approach based on a reducing reaction, hypothesizing that double bonds can be saturated by means of a reduction reaction, breaking the aromaticity, thus making coloured molecules colourless. The reductant reagent sodium metabisulfite (MBS) has been proved to be a powerful bleaching agent. Therefore, a novel treatment using MBS and an extra ingredient (Ingredient A) has been developed and is being patented. Afterwards, and to accomplish with the second objective (safety), an optimization of the treatment has been performed using an experimental design. Studying the bleaching effect and the hardness as responses, MBS concentration, pH and Ingredient A concentration were the three factors studied, searching for the highest bleaching effect while controlling the damage. The results of this optimization will be presented and discussed.

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Rapid method for the detection of exosomes as a novel biomarker for cancer diagnosis

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Keywords: *exosomes, biomarkers, magnetic particles*.

The identification of novel biomarkers represents a worldwide challenge not only for the improvement of early diagnostics, but also for patient monitoring and for the evaluation of the efficiency of a therapeutic strategy. Exosomes are nano-sized and cup-shaped vesicles [1] (Fig. 1A), which are currently under intensive study as potential diagnostic biomarkers for many health disorders, including cancer [2]. This is a growing need for sensitive methods capable of accurately and specifically determining exosome concentration. This work addresses the design of a quantitative and rapid method for total exosome counting based on magneto-actuated platforms with optical and electrochemical readout. Nanovesicles purified from breast cancer cell lines culture supernatants were used as a sorce of nanovesicles. Two different strategies were explored for the magnetic separation of exosomes: i) direct covalent immobilization on tosyl-activated magnetic particles or ii) immunomagnetic separation by antiCD9|CD24| CD44|CD54|CD63|CD81 or CD340 antibody-modified magnetic particles (Fig. 1B). Then, exosomes immobilized on the magnetic platforms were detected with antibody labeled with horseradish peroxidase for optical and electrochemical readout (Fig. 1C and 1D). Exosome counting by the magneto electrochemical biosensor provided outstanding results and analytical performance even in human serum matrix. This proof-of-concept study represents a rapid, cost-effective, and high-sample-throughput detection of exosome and a promising application in cancer diagnostics.

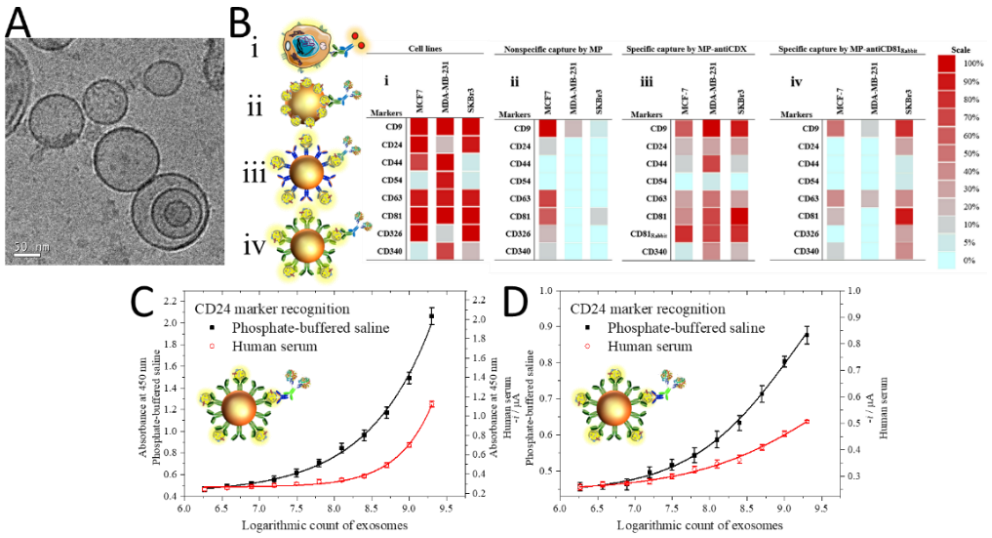

Fig. 1. (A) Cryogenic transmission electron microscopy (Cryo-TEM) of purified exosomes. (B) Surface screening markers obtained by flow cytometry for breast cancer cell lines, and their respective exosomes. (C) Optical and (D) electrochemical response of the biosensor for exosome count using MP-antiCD81$_{Rabbit}$ for immunomagnetic separation and detect by CD24 marker from SKBr3 cell line.

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Sulfonated, trifluoromethylated and carboxylated triarylphosphines. Application in biphasic hydroformylation

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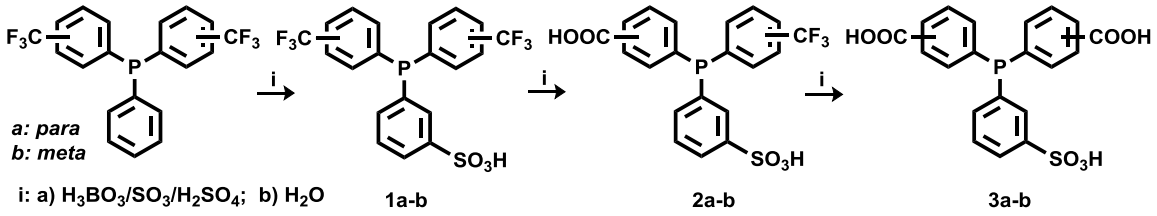
We have designed a methodology to obtain triarylphosphines containing sulfonic and carboxylic groups and, in some cases, also trifluoromethyl groups. This methodology is based on the hydrolysis of the trifluoromethyl group in phenyldiarylphosphines with oleum and boric acid [1, 2, 3]:



We have also developed an efficient method to separate and purified these phosphines when they are obtained as mixtures. Appropriate substitution allows to prepare phosphines with modulated water soluble properties (sulfonic groups), with variable acidity (CF_3 groups), as well as different amphiphilicity (through modification of the carboxylic functionality).

Some of these phosphines have been used in rhodium catalysed biphasic hydroformylation (organic solvent/ water) of vinyl acetate. The rate of hydroformylation depends on the number of trifluoromethylated groups. Hence, phosphines type **1** are more active (tof ≈ 7 min^{-1}) than type **2** (tof ≈ 4 min^{-1}), and type **3** are nearly no active under biphasic conditions (P = 30 bar CO + H_2 at 80°C; 5 ml water/ 4 ml Et_2O , vinyl acetate/phosphine/Rh =2500/20/1). Separation of the aqueous catalytic mixture allows efficient recycling of the catalyst.

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NIRS and Chemometrics applied to challenging conditions in pharmaceutics, forensics and biotechnology

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Near Infrared Spectroscopy (NIRS) is an analytical technique based on the interaction between electromagnetic radiations in the wavelength range 780-2500 nm and matter. The NIR spectrum can be considered as a "*fingerprint*" of each chemical compound or mixture of them, which contains absorption bands that are the result of overtones and combinations of the fundamental vibrations observed in the Mid-Infrared region. Additionally, NIRS of solids is sensible to the scattering effect caused by physical characteristics of the samples, therefore it provides simultaneous sensitivity to chemical and physical changes of solid samples. The fact that NIR spectra show broad and overlapped bands makes it necessary the use of Chemometrics, which implies the application of statistical and mathematical methods to such spectral data, for achieving the maximal extraction and collection of useful information from it [1]. The general objective of this doctoral thesis is developing analytical methods based on NIRS and Chemometrics in challenging conditions from the NIRS perspective, with the aim of evaluating the benefits and drawbacks of the technique in such particular cases. The following conditions have been considered: i) extended active pharmaceutical ingredient concentration ranges during granulation and tableting using the process spectrum, ii) on-site identification of new psychoactive substances during police seizing procedures and iii) inline monitoring of the production of recombinant Lipase B from C*andida antarctica* in *Pichia pastoris* using glycerol as carbon source.

i) Extended active pharmaceutical ingredient (API) concentration ranges during granulation and tableting using the process spectrum (PS),

The PS is a methodology for preparing calibration sets by adding the changes due to the manufacturing process to NIR spectra of samples prepared at the laboratory, using an algebraic procedure [2]. The PS has successfully included the process contributions during modelling in the central point of API concentration values of diverse formulations [3], however the properties of this methodology at extreme points of API concentration ranges have not been studied yet. For evaluating such properties, in this work the PS was applied to samples in the range of ± 30% of a nominal API value. Preliminary results shown that the PS performance can be affected by API concentration changes in the studied range, and classical pre-treatments are not enough to overcome this condition. The calibration transfer approach seems to be an alternative in these cases.

i) On-site identification of new psychoactive substances (NPS) during police seizing procedures

The NPS are 'legal highs' with molecular differences regarding the structures of illicit controlled drugs, whose emergence have expanded the current synthetic drugs market in a very important way [4]. The feasibility of using portable NIRS instruments for the fast identification of NPS have been demonstrated using mainly pure drugs or pure drug-related compounds [5]. Hence, the goal of this effort was to develop classification models including police seized samples during the construction of NIRS spectral libraries.

iii) Inline monitoring of the production of recombinant Lipase B from C*andida antarctica* in *Pichia pastoris* using glycerol as carbon source.

The use of new constitutive promoters and recycled carbon sources in the recombinant production of industrial proteins, such as lipases, in the cell factory *Pichia pastoris* is advantageous for improving production yields and minimizing the cost of the culture medium [6]. The capabilities of a NIR spectrometer with fiber optic coupling for immersion of a transflectance probe were employed for the inline monitoring of the fermentation mentioned in the headline. Quantitative models have been developed for Biomass, Total protein, Glycerol, Nitrogen and Activity, which have demonstrated better prediction capability during the feed batch stage than during the batch stage. The main challenges of this case were the aqueous medium (water is one of the best analytes for NIRS, consequently one of the worse solvents to work with) and the constant changes in biomass production.

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Optimised azobenzene photoswitches for reliable two-photon neuronal excitation

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Ionotropic glutamate receptors (iGluRs), the main responsible of excitatory currents in the central nervous system, can be remotely controlled by means of light-responsive molecules. This is the case of MAG ligands, which are composed of a maleimide moiety for receptor binding, an azobenzene photoswitch and a glutamate agonist (Figure 1a).[1] *Trans-cis* photoisomerisation of these compounds allows modulation of glutamate-receptor interaction, thus resulting in light-induced operation of the cell membrane ionic channels governed by iGluRs.

In our group we have rationally developed new MAG switches capable to trigger iGluRs upon 2-photon excitation with near infrared light, which should enable larger penetration depths in biological tissues with minimal biological degradation.[2] This requires high 2-photon absorption cross-sections (σ_2) as well as long *cis* state lifetime (τ_{cis}). In this presentation, new MAG compounds synthesised along these design principles are presented (**MAG$^{slow}_{2P}$** and **MAG$^{slow}_{2P_F}$**, Figure 1b), with which we have achieved up to 6-fold enhancement of the 2-photon response of iGluRs with near infrared light (Figure 1c-d).

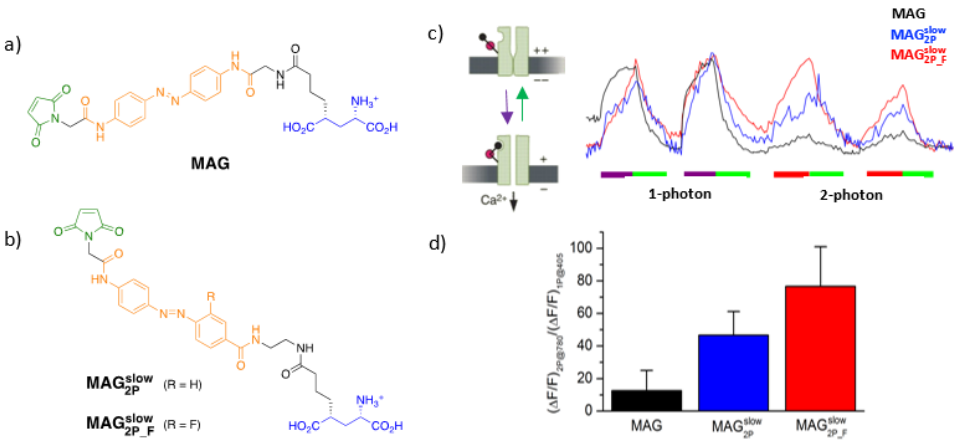

Figure 1. a-b) Structure of **MAG** and MAG-derivatives **MAG$^{slow}_{2P}$** and **MAG$^{slow}_{2P_F}$** with enhanced 2-photon absorption. c) Reversible light-induced activity of MAG-tethered iGluRs under 1-photon (405 nm) and 2-photon (780 nm) excitation. d) Average 2-photon/1-photon response of the different MAG-derivatives.

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Designing water-soluble sulfonate and arginine-rich bioconjugated Cu(II) complexes with anticancer properties. A redox-active metallic core

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Metals can offer an enormous versatility and a vast myriad of properties to be tuned. The inherent side effects of Pt compounds and the acquired resistance to Pt by some tumour cells triggered the research on improved Pt strategies and on other non-Pt metallic drugs. During the last 30 years, Ru, Ir, Pd, Fe or Cu have appeared as promising alternatives to overcome the drawbacks encountered with Pt compounds.[1] Beyond all of them, and mainly during the last decade, Cu complexes have awakened strong interest as therapeutic agents.[2] Copper is a biologically active metal ion that displays a crucial role in an enormous variety of biological functions. Two important features make it attractive to be used in chemotherapy: its nature as an endogenous metal –which may imply fewer side effects than other exogenous metals- and its Cu(II)/Cu(I) redox pair –which can promote reactive oxygen species (ROS) generation.[3] The production of ROS is not only reported to cause cellular damage, but also to offer a putative discrimination between healthy and non-healthy cells. Considering that cancer cells exhibit abnormal levels of ROS and that they show higher vulnerability to ROS level changes than healthy cells do, the modification of those levels represents a unique opportunity to selectively target cancer cells.[4]

We have synthesized and characterised three novel dimeric Cu(II) complexes that have been proved to be active against HeLa and MCF7 cancer cells. They are based on tridentate *N,O*-donor aromatic planar ligands, specifically designed with the idea of promoting Cu(II)/Cu(I) redox interconversion in biological conditions. In vitro assays highlight the high potentiality of the metallic core to undergo significant ROS generation inside HeLa cancer cells. However, one of the main drawbacks faced was their poor solubility. Therefore, our recent work has been focused on the functionalisation of the ligands to improve their solubility while maintaining the same Cu(II) coordination environment, i.e., the high redox activity already observed. In this particular case, two different strategies have been explored to enhance the activity of the complexes: (i) adding a sulfonate group, based on its pK_a and its biological relevance[5] and (ii) using arginine-rich peptides, to specifically improve their penetrability into tumors.[6]

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From Surface to Nanoparticles: Ruthenium Oxide (RuO_2) Systems and Their Interaction with Water

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Keywords: *Ruthenium oxide, surfaces, nanoparticles, DFT, VASP, water splitting*

The formation of molecular oxygen from the oxidation of water is the most challenging step in the water splitting process. To overcome this critical semi-reaction, heterogeneous catalyst or nanoparticles based on metal oxides have been used. In particular, *ruthenium oxide* based materials have been shown to be good candidates, due to its unique redox surface chemistry and conductivity. [1]

In this contribution, DFT calculations with periodic boundary conditions [2] have been carried out to analyze water adsorption on different RuO_2 based materials and the water electrochemical oxidation assisted by these materials. First, we have analyzed the water adsorption energy onto the most stable RuO_2 surfaces paying special attention in to the effect of water coverage. Second, *Wulff construction* [3] approach has been used to build up RuO_2 nanoparticles and analyze how water adsorption is influenced by the nanoparticle shape and size. Results show that water coverage, surface morphology and temperature play an important role in the degree of water dissociation on the surface, which is characterized by the formation of $[H_3O_2]^-$ units. [4] Moreover, comparison between surface and nanoparticle models reveals an important influence of the size of the material. This is particularly relevant on the water oxidation reaction since the potential that has to be overcome decreases with the decrease of the nanoparticle size.

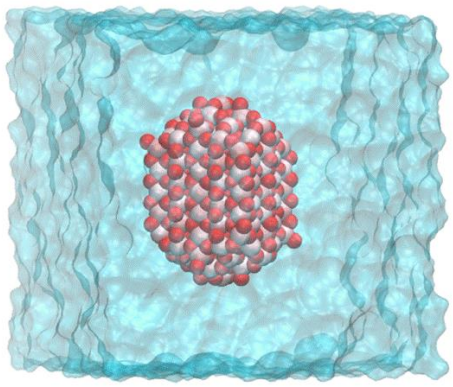

Figure 1. Ruthenium Oxide Nanoparticle (1.20 nm) solved in Water

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Potential radiopharmaceuticals: "from synthesis to pre-clinical trials"

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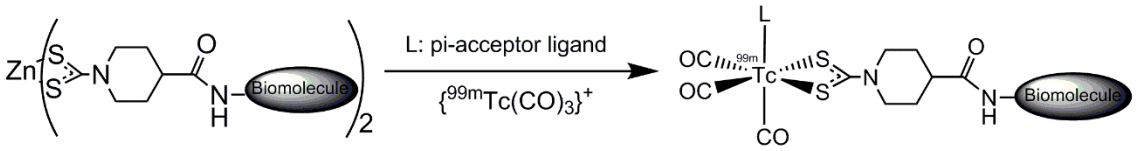
Probably, the best-known techniques in medicinal diagnosis currently used in hospitals are NMR, X-rays or ultrasounds. However, there are other powerful techniques that can provide structural and functional information of a patient. Among them, nuclear medicine is a medical specialty that it has been growing during the last decades and nowadays it has a very important role in medical imaging. Briefly, nuclear imaging applies radiocompounds (radiopharmaceuticals) that can specifically being accumulated to a target organ, tissue, etc… providing morphological or metabolic information of this organ. Apart from being non-invasive techniques, they are the only ones capable to detect biochemical and physiological abnormalities before the appearance of anatomical changes in the organism [1].

My research group has been working for many years in a strategy based on a transmetallation reaction between a zinc precursor, which contains a biological active molecule, a technetium-99m synthon ($\{^{99}mTc(CO)_3\}+$) useful for SPECT and a monodentate π-acceptor ligand (Scheme 1)[2].



Scheme 1. Transmetallation reaction for the preparation of potential radiopharmaceuticals

The strategy leads to the radiosynthesis of a potential radiopharmaceutical with high specific affinity without the need of further purification after the synthesis. It is a consequence of the high ratio between radiolabelled biomolecules and unlabeled biomolecules. In our approach, we achieve to decrease the concentration of the unlabeled molecules by means of a zinc precursor which contains the biomolecule that presents a very low solubility in water. Thus, the number of unlabeled biomolecules at the end of the reaction is lower than other methods. It should be highlighted that, despite the low concertation of the zinc precursor, the reaction is completely feasible due to thermodynamic reasons.

In my work I had the chance to have a great overview from the synthesis of some potential radiopharmaceuticals to the study of their behavior in in vitro and in vivo experiments.

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Amperometric rGO-Nanocompostives Electrochemical Sensors Functionalized With Metal Nanoparticles

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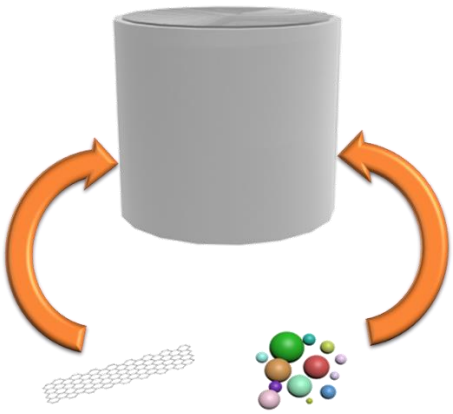
Since the discovery of graphene, this material has captured great interest among scientific community. Graphene is a two-dimensional sheet of carbon atoms in a hexagonal configuration with atoms bounded by sp^2 bonds. Among others carbon materials such as graphite, carbon nanotubes or nanodiamonds, graphene has been an ideal material in electrochemistry due to his excellent 2D electrical conductivity, high surface area and the low-cost mass production[1]. Nanocomposites are a class of materials in which different nanomaterials in an organic polymeric matrix are dispersed in order to improve the structures and properties of the polymer effectively. Reduced graphene oxide (rGO) has been synthesized following the Hummer's method for the preparation of rGO-nanocomposites electrodes containing an epoxy resin as an insulating phase[2]. The functionalizaton of graphene with metal nanoparticles (MNPs) such as Ag, Au and AuPd hybrid metal. These NPs integrated in amperometric sensors show an excellent improvement for the electrochemical catalysis of H_2O_2 oxidation. In this sense, these materials could be functionalized with different kind of oxidases for multiple analyte deteccion.



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Optimisation Studies of Hard Carbon Negative Electrodes for Sodium Ion Batteries

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The development of a sodium ion battery technology analogous to lithium ion is currently attracting interest for cost and sustainability issues. Hard carbons are currently the most promising negative electrode materials despite some drawbacks to resolve in order to get optimum performance.

Hard carbons were prepared from different precursors (cellulose, lignin and phenolic resin) and under different pyrolysis and processing conditions using both laboratory and industrially adapted syntheses protocols. Their microstructure (surface area, porosity, tapped density etc.) was characterized and efforts were made to correlate it with the electrochemical performances. The results obtained point at surface area as a key factor to determine reversible capacity and good cyclability. The surface area is found to depend on the precursor composition and the temperature and inert gas flow during the pyrolysis process.

Optimum performance (higher reversible capacity) is achieved for hard carbons prepared at 1100-1200°C under high argon flows.

Applications of the cyclobutane scaffold in new cell penetrating agents for drug delivery

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The cyclobutane moiety can be used as a conformational restriction element in a wide variety of products providing both rigidity and chiral centers of known and unambiguous absolute configuration. In the current PhD Thesis, this scaffold has been used to design and synthesize various new families of Cell Penetrating Peptides (CPPs). Moreover, their biological evaluation has been carried out using two different biological systems: *HeLa* cells and *Leishmania* parasites.

These peptides incorporate derivatives of γ-amino-*L*-proline functionalized with N^{α}-side chains containing guanidinium groups in alternation with cyclobutane-containing γ-amino acids. The influence of the stereochemistry and the length of the peptide have been studied regarding their cell-uptake ability. The introduction of cyclobutane moieties reduces the characteristic toxicity of peptides with guanidinium groups by combining charge and hydrophobicity and confers rigidity to the final structure (Figure 1).[1,2]

The studied peptides are efficient as penetrating agents for *HeLa* cells and *Leishmania* parasites, especially in some cases where they are twice as good as reference peptide TAT_{48-57}. Moreover, the toxicity of the peptides has been evaluated in these systems, obtaining good values of survival in both. Further studies with a drug conjugated to the peptide are being carried out to check their behavior as antileishmanial agents.

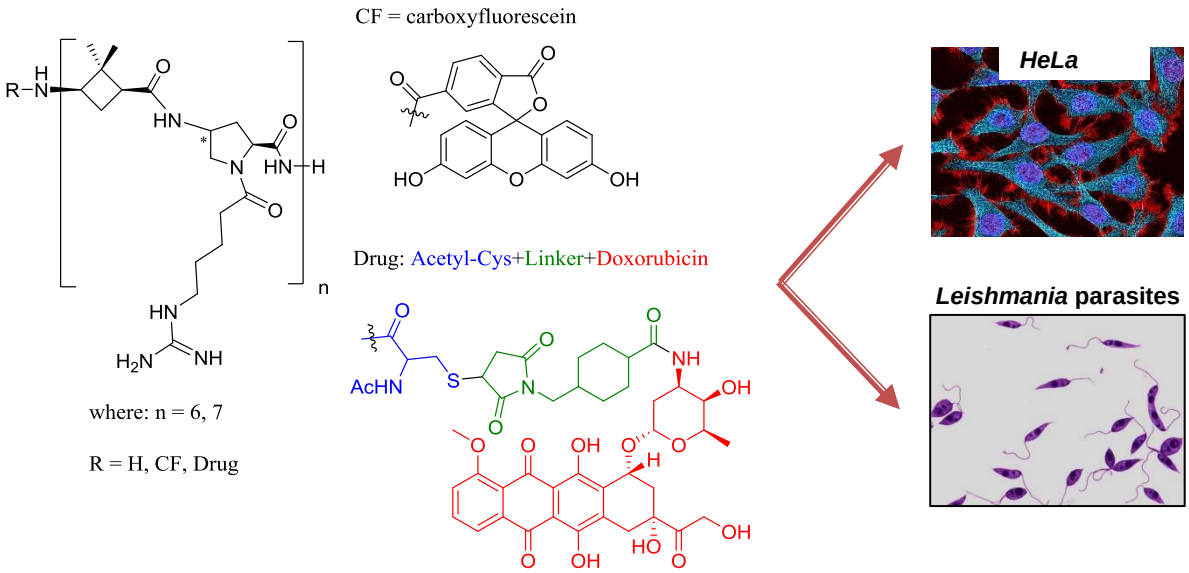

Figure 1. Structure of synthesized and evaluated hybrid CPPs and systems used in the study.

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Chemoselective polymerization using difunctional monomers: Towards polyacrylates with pendant cyanoacrylate moieties

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Instant adhesives, or so-called 'super glues' are well known consumer products sold all around the world. These products are derived from the chemical class of cyanoacrylates (CAs) and undergo extremely rapid nucleophilic/anionic polymerization [1]. The appeal of these products is their speed, however, they have limited applications since are not intended for structural purposes where crosslinked polymer networks are demanded.

Herein we describe a new approach to achieve reactive (meth)acrylic polymers bearing pendant unreacted CA, which would undergo crosslinking and thus enhance properties of the cured adhesives.

First attempts to obtain polymers with pendant CA require access to new hybrid divinyl molecules (uniquely available through a patented Afinitica Technologies synthesis) [2]. These CA hybrid molecules bear additional acrylic (CAA) or methacrylic (CAMA) functional groups (Figure 1). In principle these should have preferred and independent polymer initiation mechanisms.

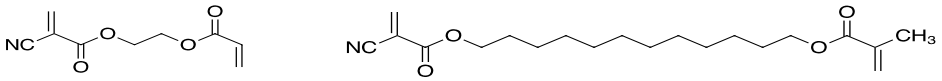

Figure 1: Divinyl hybrid molecules containing cyanoacrylate and acrylate/methacrylate

We describe the facile chemoselective polymerisation of cyanoacrylate functions in CAA and CAMA molecular hybrids wherein the cyanoacrylate function can be easily polymerised with nucleophilic initiators while the acrylic function remains unreacted leading to polymers that have a poly-CA backbone with pendant (meth)acrylic functional groups. However, the reverse scenario where the (meth)acrylic functions are copolymerized with the acrylic functional groups of either CAA or CAMA by radical initiation leading to polymers with pendant CA groups has thus far not been possible to achieve.

Current effort is directed to understanding how to encourage selectivity, for example through the search for suitable 'partner' monomers that may allow for better control in copolymerisations. So-called captodative (CD) monomers, which show interesting propensity for moderation in copolymerisation due to their highly stable radical formation, may be suitable candidates. We are currently examining the copolymerisation of CD monomers with CA-hybrids.

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The mechanism and adsorption study of Pine biomass and pyrolyzed Pine loaded with TiO_2 in aqueous solution

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Pine biomass and pyrolyzed pine loaded with TiO_2 (Pine/TiO_2) have been used as sorbent for the removal of heavy metal ions from aqueous solution. A single-element system and multi-element system were used to removal heavy metals. The multi-element system composed by a mixture of Cr(III), Cd(II), Cu(II) and Pb(II) ions was used to simulate a realistic case of waste water polluted with heavy metals case for adsorption. Different parameters of adsorption processes were optimized in batch systems (pH of the solution, the initial concentration and the contact time). Surface morphology of the adsorbents were analyzed using scanning electron microscopy(SEM) and Fourier transform infrared spectroscopy(FT-IR). Pine showed better adsorption capacity for all heavy metals in single-element system, on the other hand Pine/TiO_2 increased the adsorption in multi-element system, especially to Cu (II) and Pb(II) with 130 and 98.4µmol/g, respectively. The results of X-ray absorption spectroscopy (XAS) shows that the adsorption mechanism of Pb is ion exchange with low concentration of multi-element system. The adsorption mechanism of Cr(III) is compleaxion. Pine/TiO_2 as a promising cost-effective and environmental friendly material, especially in multiple systems

Key words: pyrolysis, heavy metals, TiO_2, XAS

A novel potentiometric microsensor for real-time detection of Irgarol using the ion-pair complex [Irgarol-H]+[Co(C2B9H11)2]

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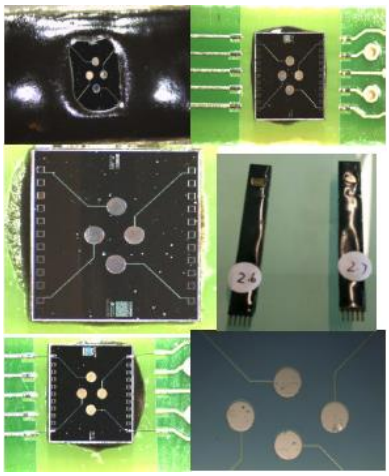
Ion pair complexes of Irgarol with metallacarboranes have been synthesized for use as ion selective electrodes for the potentiometric detection of the notorious algaecide, Irgarol.[1] Potentiometry is a simple and effective technique for the rapid determination of analytes. The protonated amine groups were prepared with $Cs[Co(C_2B_9H_{11})_2]$ to form ion pair complexes. This ion pair complex acts as an ionophore and in conjunction with a polymer matrix (like PVC) and a suitable plasticizer (like NPOE, DOP, DOS etc) can be used for the potentiometric detection of the desired antibiotic (in this case Irgarol).

Metallacarboranes like $[Co(C_2B_9H_{11})_2]^-$ have been known to show very good performances as an Ion selective electrode membrane lipophilic anion additive.[2] Also cobaltabis(dicarbollide) [3,3′-$Co(1,2\text{-}C_2B_9H_{11})_2]^-$ has shown to provide a high stability to the polymer when used as a dopant anion with a conducting polymer like Polypyrrole[3]. The ISEs prepared using cobaltabis(dicarbollide) [3,3′-$Co(1,2\text{-}C_2B_9H_{11})_2]^-$ also show low charge density and produce C_c–H···H–B and B–H···H–N dihydrogen bonds, and C_c–H···O (C_c=Carbon cluster) hydrogen bonds which play an important role in the stability of the membrane[4].These factors have been used to make microelectrodes having a conducting polymer layer of Cobaltabis(dicarbollide) and Polypyrrole while the ion pair complexes of the aforementioned protonated amine groups act as ionophores. These devices have shown good selectivity and sensitivity during the potentiometric detection of this antibiotic.



This is a novel method for the detection of these compounds in sea water and will be useful in finding out the levels of these toxic compounds in sea water and ultimately aiding in its purification

Acknowledgements:

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Sea on a chip Project (FP7-KBBE) under the reference 614168.

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Printing technologies for biotechnological and environmental sensing applications

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Modern manufacturing processes have left widespread hazardous compounds across the globe. The over exposure of workers involved in decontamination processes in sewage treatment plants and the direct impact in rivers and streams has triggered the alarms. Therefore, production of durable, fast, and robust sensing platforms to track contaminants across the environment has become a global concern. Nowadays, breakthrough technologies, such as microfabrication and printing techniques, have led to more automated sensor fabrication procedures. With these technologies, typical requirements, such as reproducibility and repeatability are meet in a miniaturized fashion, which in turns allow them to be used in broader situations. Among others, printing technologies have emerged as a standard method for production of low-cost sensing platforms. Herein, the fabrication and characterization of different electrochemical/optical detection-based platforms for quantification of sulphate and sulphide have been developed. Considering all the current challenges in the fabrication of sensing platforms for environmental and biotechnological screening applications, this appealing technology could constitute a new paradigm in the production of functional monitoring devices.

Glycine polymerization catalyzed by the TiO_2 (101) anatase surface

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The interaction of biomolecules with mineral surfaces is a topic of extraordinary relevance, due to its broad application in many fields[1]. In particular, the adsorption of amino acids on mineral surfaces is of interest in the prebiotic chemistry field, because they can protect and concentrate amino acids, and also catalyse the condensation reaction among them to form oligopeptides[2]; both experimental and computational works confirm this theory [3, 4]. , Within this context titania acting as adsorbent surface plays a fundamental role due to its natural large abundance[5]. Several reactions about the peptide bond formation between two glycine molecules adsorbed on the TiO_2 (101) anatase surface were studied, by means of periodic DFT calculations using the VASP code (see Figure 1). In particular, we decided to focus on three main aspects: i) the effect of the surface as reaction catalyst, ii) the presence of water molecules that may assist the proton transfer between the amino group and the carboxyl group and iii) the adsorption states of the initial amino acids.

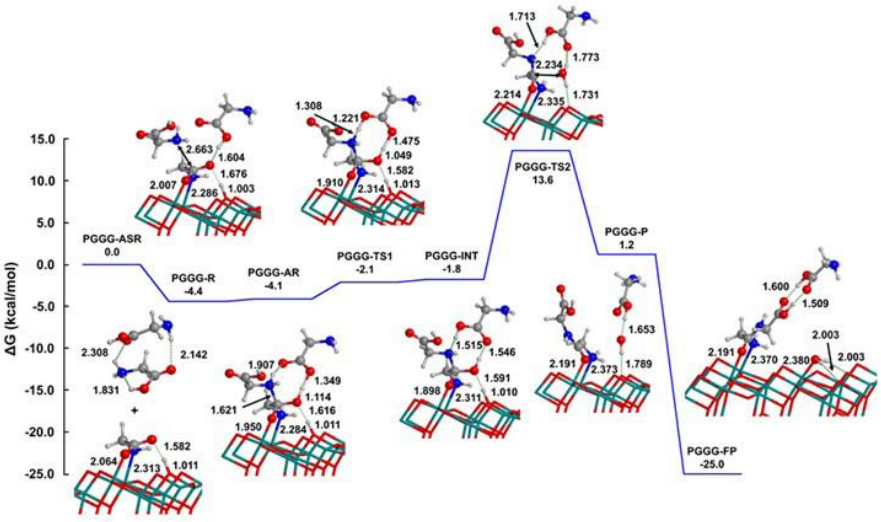

Figure 1: Relative free energy profiles (T = 298 K) at PBE0-D2*//PBE-D2* theory level for the glycine assisted reaction: Gly + Gly + Gly → Digly + Gly + H_2O

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