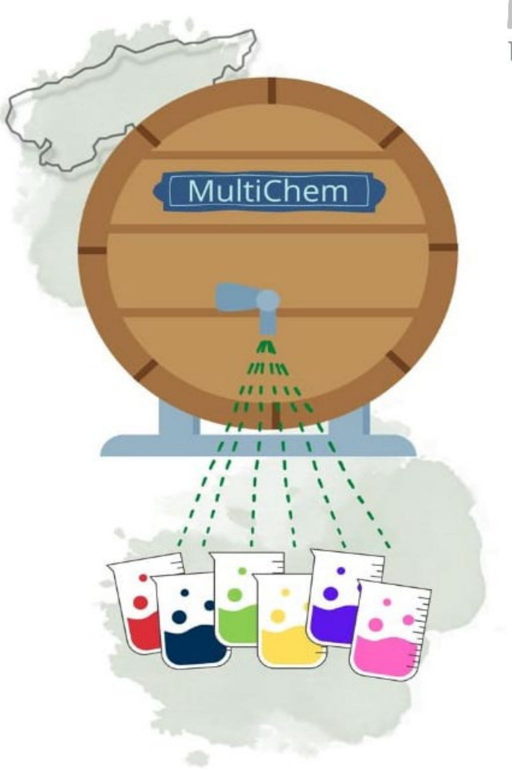
I PhD Multidisciplinary Chemical Congress



BOOK OF ABSTRACTS

January 19-20th, 2023
Escuela Politécnica de Ingeniería de Gijón (EPI)
University of Oviedo

INDEX

WELCOME

We would like to present the first edition of the **PhD Multidisiciplinary Chemical Congress** aimed at PhD students in Chemistry or any related area, which will take place on January 19 and 20, 2023 at the Escuela Politécnica de Ingeniería de Gijón, Gijón (Principality of Asturias), University of Oviedo (Spain).

In this congress the doctoral students are the main actors both in its organization and in its development. It will generate a multidisciplinary space in which we can actively participate in disseminating our scientific production and promote collaboration between the different branches of chemistry.

This congress, which is under the umbrella of the Asturias Territorial Section of the Royal Spanish Society of Chemistry, is born with the aim of making visible the Chemistry that is done in our laboratories by the hand of the younger generations.

COMMITTEES

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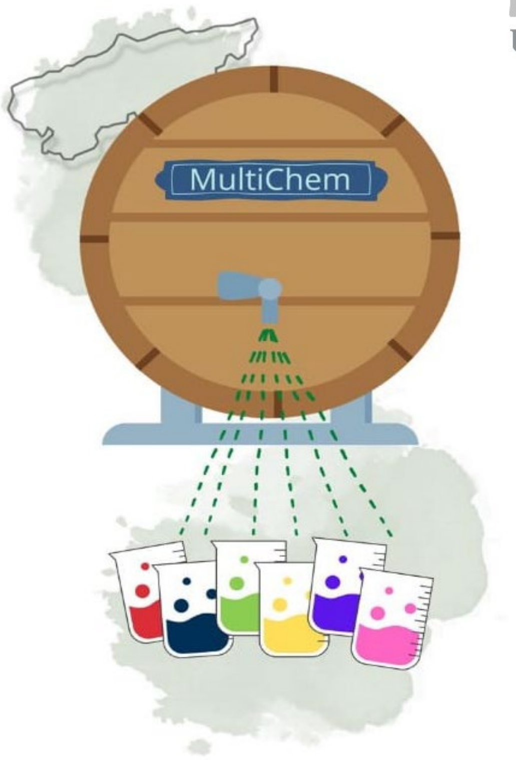

PROGRAM

Thursday, January 19th

9:00-9:15	**Opening Ceremony**
9:15-11:35	**Morning session 1** Chairperson: Mª Jesús Lobo Castañón (University of Oviedo)
9:15-10:15	**Plenary Lecture (PL-1)** Nanobiosensor Devices for Ultrasensitive Diagnostics at the Point-of-need Laura M. Lechuga Gómez Catalan Institute of Nanoscience and Nanotechnology (ICN2-CSIC)
10:15-10:30	**Scharlab**
10:30-10:50	**Keynote A** Using large 18-membered macrocycles for the complexation of metals with potential radio-pharmaceutical applications Charlene María Harriswangler CICA-University of A Coruña
10:50-11:05	**Oral 1** Signal drift in electrochemical, aptamer-based (E-AB) sensors: understanding its mechanism and future challenges Miguel Aller Pellitero Johns Hopkins University
11:05-11:20	**Oral 2** Main group mechanochemistry: challenges and opportunities for a sustainable society Javier Fernández Reynes University of Oviedo
11:20-11:35	**Oral 3** Impact of chelate cooperativity on the supramolecular structure of self-assembled nanotubes Marina González Sánchez Autonomous University of Madrid
11:35-12:20	**Coffee break – Poster session (PO1-56)**
12:20-13:40	**Morning session 2** Chairperson: José Manuel Recio Muñiz (University of Oviedo)
12:20-12:35	**Oral 4** Understanding ruthenium-prompted amine fixation: deep insight on Bonding Evolution Theory Daniel Barrena Espés University of Oviedo
12:35-12:50	**Oral 5** Optimizing the process variables for microwave-induced synthesis of iron aerogels Judith González Lavín Institute of Carbon Science and Technology, INCAR-CSIC
12:50-13:10	**Keynote B** Influence of vibronic instabilities on the geometry and properties of layered materials Inés Sánchez de Movellán Sáiz University of Cantabria
13:10-13:25	**Oral 6** Determination of methylmercury and inorganic mercury in human hair samples of individuals from Colombia by double spiking isotope dilution and GC-ICP-MS Laura Suárez Criado University of Oviedo
13:25-15:30	**Lunch**

15:30-16:15 **Flash poster (FP1)**
Chairperson: Marina Ramos Martín

Paula Gómez Meijide (University of Oviedo)	Prostate cancer diagnosis by PSA detection using new electrochemical aptasensors
Clara de Lorenzo González (University of Oviedo)	Hydrogels-based systems for the controlled release of therapeutic agents: an innovative treatment for osteoarthritis
Nayara Carral Sainz (University of Cantabria)	Second principles density functional theory models: a procedure to obtain their tight-binding parameters automatically
Daniel Núñez Díaz (University of Oviedo)	Effect of landfill leachate age on ultrafiltration performance
Ángela Arnosa Prieto (University of Santiago de Compostela)	Effect of Interleukin 4 loaded Citrate Coated Iron Oxide Nanoparticles on Macrophage Polarization for Bone Regeneration
Toraya Fernández Ruiz (University of Cantabria)	Modelling Optical Phenomena via Real-Time TD-DFT using Second-Principles: Measuring the effect of electron-hole interactions
Silvia Vázquez Díaz (Center for Cooperative Research in Biomaterials (CIC biomaGUNE) País Vasco)	Protein-nanoclusters as effective electrocatalyst for the production of inkjet printed paper analytical devices
Montserrat Redondo Velasco (University of Oviedo)	Determination of Chlorine-containing compounds by GC-ICP-MS/MS in plastic-based pyrolysis oil samples
Lucía Pola Fernández (University of Oviedo)	Kraft lignin as a source of carboxylic acids by wet oxidation
Miriam López García (Institute of Carbon Science and Technology, INCAR-CSIC)	A freeze-casted Ni/Fe graphene oxide aerogel as a catalyst for the electrolysis of water
Cristina Méndez López (University of Oviedo)	Halogen determination in liquid samples via optical emission spectroscopy: towards online analysis
Rubén García Soriano (University of Oviedo)	Phosphane and quinoline functionalized amidinato-type heavier tetrylenes: A new class of ligands
Raúl Llamas Unzueta (Institute of Carbon Science and Technology, INCAR-CSIC)	Stacked Archimedean spirals reactor with porous carbon walls, made from 3D printed sacrificial PLA moulds
Nieves García Ledesma (University of Salamanca)	One-Pot diastereoselective synthesis of indolizidine and pyrrolo-[1,2-a]azepine heterocycles

16:15-17:05 **Afternoon session 1**
Chairperson: Rosa Mª Sainz Menéndez (University of Oviedo)

16:15-16:30 **Oral 7**
Development of a paste extruder system and production of Ni-electrodes by diw for water splitting
Pablo Rodríguez Lagar
Institute of Carbon Science and Technology, INCAR-CSIC

16:30-16:45 **Oral 8**
Albumin-based nanomaterials: a novel treatment for triple-negative breast cancer
Victoria García Almodóvar
King Juan Carlos University

16:45-17:05 **Keynote C**
Determination of endogenous proteins in individual cells from an in vitro model by elemental mass spectrometry
Paula Menero Valdés
University of Oviedo

17:05-17:50 **Coffee break – Poster session (PO1-56)**

17:50-18:35 **Afternoon session 2**
Chairperson: Alejandro Presa Soto (University of Oviedo)

17:50-18:05 **Oral 9**
Discrimination of TNT and its metabolites in the environment using voltammetric sensors, modified with molecularly imprinted polymers
Yohana López Aparicio
Autonomous University of Barcelona

18:05-18:20 **Oral 10**
Scalable divergent synthesis of diterpenoid pyrones
Olaya García Pedrero
University of Oviedo

18:20-18:35 **Oral 11**
Perylene-based chromonic self-assemblies for the preparation of hierarchically porous silica and carbon nanofibers
Adrià Pérez Calm
Institute of Advanced Chemistry of Catalunya (IQAC)-CSIC

18:35-19:20 **Flash poster (FP2)**
Chairperson: Daniel Núñez Díaz

Andrés Suárez Priede (University of Oviedo)	ICP-MS based characterization of biogenic SeNPs and evaluation of their potential antibacterial activity
Juan Rivas-Santisteban (National Biotechnology Center (CNB-CSIC))	Characterization of a chemical bias shaping microbial functional evolution
Leonardo Amaral (King Juan Carlos University)	Magnetic MoS_2 based nanocomposites for the photodegradation of pollutants
Ana da Lama Vázquez (CICA-University of A Coruña)	One-step synthesis of BODIPY dyes and analogues under microwave irradiation
Alejandro Rodríguez Penedo (University of Oviedo)	Determination of GFAP biomarker in human serum using metal nanoclusters as label by elemental mass spectrometry and cyclic voltammetry
Raquel Pérez Guevara (CICA-University of A Coruña)	Synthesis of benzannulated spiroketals by indium-catalyzed intramolecular double dihydroalkoxylation of alkyne diols
Helena Pérez del Pulgar Villena (King Juan Carlos University)	A three-pollutant simultaneous photodegradation. $BiOX_xY_{1-x}$ (X=Br or Cl; Y=I) as a photocatalytic solution for water treatment
David Valero Calvo (University of Oviedo)	Detection of MMP-9 biomarker using nanochannels
Marcos López Aguilar (University of Oviedo)	Design of a hybrid one-pot tandem combination of the Cu(II)-catalyzed oxidation of alcohols with an enantioselective organocatalyzed aldol reaction
David González Lizana (King Juan Carlos University)	Very efficient organo-zinc scorpionates for the CO_2 fixation into a variety of cyclic carbonates
Helena Fernández Piedra (University of Oviedo)	Halogen-bonding assisted generation of vinyl radicals: stereoselective cross coupling between thiols and vinyl halides
Lourdes del Álamo Rodríguez (Complutense University of Madrid)	Supramolecular self-assembly of metal-metal bonded species
Dario Coto Menéndez (University of Oviedo)	Catalytic cyclopropanation reactions with α-silyl-, germanyl- and stannyl carbenes generated from cyclopropenes

Friday, January 20th

9:00-10:50	**Morning session 3** Francisco Calderón Celis (University of Oviedo)
9:00-9:20	**Keynote D** Effect of H_2S in biogas composition on the production of H_2 by sorption enhanced steam reforming (SESR) Alma Capa Tamargo Institute of Carbon Science and Technology, INCAR-CSIC
9:20-9:35	**Oral 12** Development of new pH-responsive delivery systems Isabel Coloma Manjón-Cabeza Complutense University of Madrid
9:35-9:50	**Oral 13** MD and DFT combined simulations Jorge Suárez Recio University of Oviedo
9:50-10:05	**Oral 14** Development of carbon materials for Na-ion capacitors Sara Payá González Institute of Carbon Science and Technology, INCAR-CSIC
10:05-10:20	**Oral 15** Graphene aerogels as nanomaterials for electrochemical detection of biomarkers Mario Sánchez Suárez Institute of Carbon Science and Technology, INCAR-CSIC
10:20-10:35	**Oral 16** Compositional similarities and differences between North West Africa (NWA) 2975, 10628 and 1950 Martian Shergottites Iratxe Población Concejo University of País Vasco (EHU/UPV)
10:35-11:35	**Coffee break – Poster session (FP1+FP2)**
11:35-13:40	**Morning session 4** Chairperson: Félix Rodríguez Iglesias (University of Oviedo)
11:35-11:55	**Keynote E** An original way to synthesize (*Z*)-*β*-silylenamides by silylium-catalyzed carbosilylation of ynamides Paz Yepes García University of Oviedo
11:55-12:10	**Oral 17** TiO_2/SnO_2 – silver clusters hybrid nanomaterials for catalytic photodegradation of micropollutants María Moreno Pérez University of Santiago de Compostela
12:10-12:25	**Oral 18** Development of on-site sensors for quality control in agri-food Candela Melendreras García University of Oviedo
12:25-12:40	**Oral 19** “Vermellogens” and the development of CB[8]-based supramolecular switches using pH-responsive and non-toxic viologen analogues Liliana Inés Barravecchia Prado CICA-University of A Coruña
12:40-12:55	**Oral 20** The enhancing effect of iron on the activity of Ni and Ni/Fe graphene-based catalysts for the electrolysis of water María González Ingelmo Institute of Carbon Science and Technology, INCAR-CSIC

12:55-13:40	**Plenary Lecture (PL-2)** Chemistry facing the challenges of our era Amador Menéndez Velázquez Idonial
13:40-14:00	**Closing ceremony**

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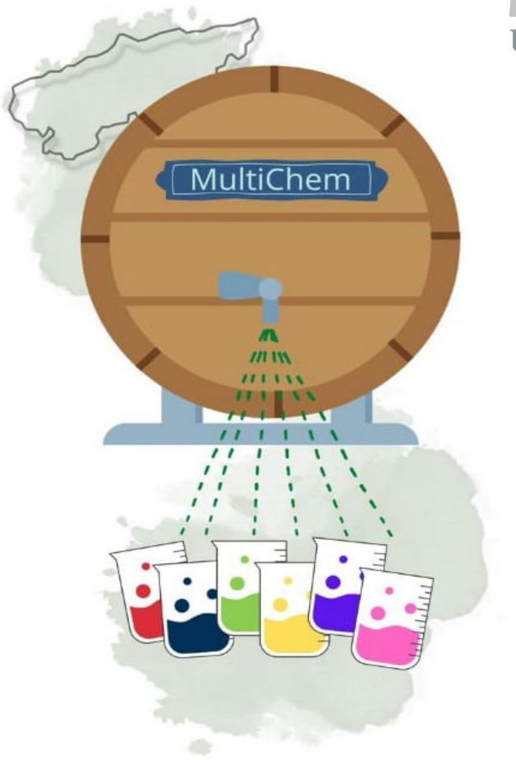

PLENARY LECTURES

PL-1: Nanobiosensor Devices for Ultrasensitive Diagnostics at the Point-of-Need

Laura M. Lechuga

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Keywords: Biosensors, Biofunctionalization, Nanoplasmonics, Label-free diagnostics.

COVID-19 pandemics has evidenced the urgent need of having portable diagnostic tools that enable rapid testing and screening of the population with sensitivity and specificity levels comparable to laboratory techniques. Biosensor technology is one of the best prepared to tackle the challenging goal of offering fast and user-friendly diagnostics tests than can be employed at the point-of-need. In particular, nanophotonic biosensors can provide sensitive, reliable and selective analysis, while reducing test and therapeutic turnaround times, decreasing and/or eliminating sample transport, and using low sample volume. Our main objective is to achieve ultrasensitive Point-of-care (POC) platforms for label-free analysis using nanophotonics biosensing technologies and custom-designed biofunctionalization protocols, accomplishing the requirements of disposability and portability.

We have demonstrated cutting-edge nanophotonic biosensors based on Nanoplasmonics and in Silicon photonics technologies that enable ultrasensitive analysis of body fluids in few minutes. By custom tailoring the biochemistry of the sensor biochips, our POC nanophotonic biosensor technology can perform direct detection of proteins, genetic biomarkers or pathogens within <15 min, with high sensitivity and selectivity. The diagnostic potential has been demonstrated and validated among others, for the drug monitoring of anticoagulants in plasma, antibiotic allergy diagnosis in plasma, early cancer diagnosis (colorectal and lung cancer) and bacterial, and viral infectious diseases [1-3]. During COVID-19 pandemic, our POC biosensor has been fully validated with hundreds of clinical samples for the direct detection of anti-SARS-CoV-2 immunoglobulins in COVID-19 patients, confirming excellent diagnostic performance [4].

Our nanophotonic biosensor approach paves the way for modern decentralised disease diagnostics. The nanobiosensor POC devices could be employed by non-expert personnel at the bed-side of patients and could have a strong impact in guiding quick medical decisions across various clinical scenarios.

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[4] O. Calvo-Lozano, L.M. Lechuga. Anal. Chem. **94**, 2, 975-984 (2022)

PL-2: Chemistry Facing the Challenges of Our Era

Amador Menéndez Velázquez

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Keywords: solid-state lighting (SSL), white light-emitting diode (WLED), rare-earth-free luminescent materials, luminescent organic materials, spectral converters.

Chemistry is a crucial tool to face some of the great challenges of our era, such as those related to the energy sector or human health. Regarding photovoltaic solar energy, a promising technology is the so-called luminescent solar concentrator. A luminescent solar concentrator (LSC) consists of a piece of glass or plastic plate coated with luminescent centers that absorb sunlight and emit it at a longer wavelength. A substantial part of the longer-wavelength light is trapped by total internal reflection and guided to the edges of the LSC plate, where it is absorbed by small area photovoltaic cells. LSCs provide an exciting new approach to harvest solar energy in buildings and mobile electronics. By converting windows and displays into LSC waveguides, it is possible to transform these passive surfaces into energy harvesting devices.

Spectral conversion or spectral modification is the process of altering the spectral distribution of light. Luminescent solar concentrators provide a way for shifting the spectral distribution of the sunlight in order to have more photons with the required energy to match the band gap of the solar cell. Spectral modification has also shown promise as an effective method of improving alga growth, the generation of green hydrogen, the design of healthy white light-emitting diodes (WLEDs) and advanced ophthalmic lenses.

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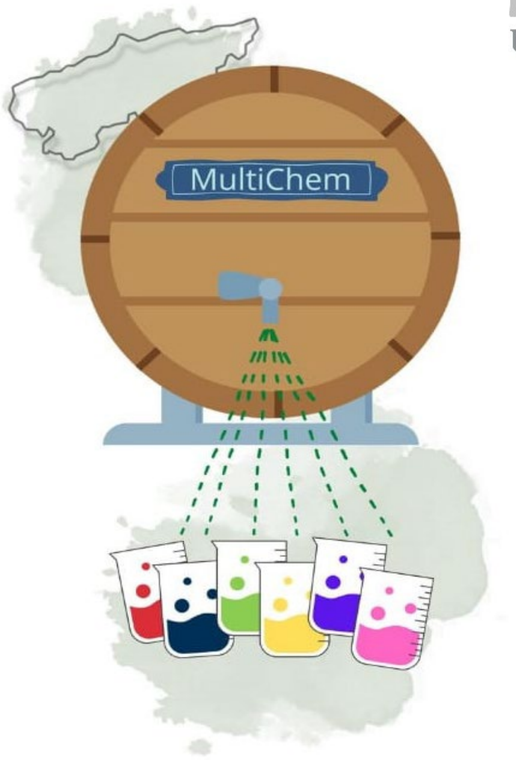

KEYNOTES

KN-1: Using Large 18-Membered Macrocycles for the Complexation of Metals with Potential Radiopharmaceutical Applications

Charlene Harriswangler[1], Isabel Brandariz-Lendoiro[1], Laura Valencia[2], David Esteban-Gómez[1], Carlos Platas-Iglesias[1]

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Keywords: coordination chemistry, radiometals, radiopharmaceuticals, macrocycles.

The use of coordination compounds in medicine allows taking advantage of interesting properties of metallic elements while avoiding possible issues associated with their toxicity. It is therefore essential to find ligands that form stable complexes with the metals of interest to evade the liberation of the metal ion inside the body when these complexes are used. A possible field of application of these complexes is radiopharmacy as there is a large number of metallic elements that possess radioactive isotopes with different applications depending on the type of radiation emitted. Elements such as La, Pb and Y, among others, present isotopes that can be either used for PET or SPECT imaging and even therapy.

In this work, ligands derived from an 18-membered macrocycle (Figure 1) and their corresponding metal complexes have been synthesized and fully characterized. Detailed computational, physico-chemical and radiolabeling studies were carried out to evaluate the potential of the chelators and their corresponding metal complexes as a part of radiopharmaceutical compounds. The results of these studies showed that, overall, these macrocyclic ligands present favorable properties for the preparation of new radiopharmaceuticals based on different metal cations in terms of high stability of the resulting complexes and fast complexation of the metal ions.

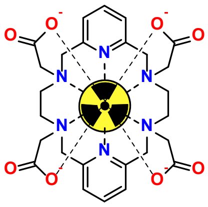

Figure 1. Structure of one of the ligands presented in this work

Acknowledgments: Ministerio de Ciencia e Innovación (PRE2020-092888 and PID2019-104626GB-I00) Xunta de Galicia (ED481A 2021/070), Centro de Supercomputación of Galicia (CESGA) and CACTI (Universidade de Vigo).

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KN-2: Influence of Vibronic Instabilities on the Geometry and Properties of Layered Materials

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Keywords: layered materials, symmetry, orthorhombic instability, Jahn-Teller effect

During the last two decades a great deal of attention has been focused on layered systems containing transition metal (TM) compounds such as Cu^{2+}, Ag^{2+} or Mn^{3+} surrounded by anions (F^-, Cl^-, O^{2-}). This trend is motivated by the discovery of a wide range of new properties and effects such as high-T_C superconducting states, 2D magnetism or photovoltaic applications of layered hybrid materials [1]. In general, layered systems display low symmetries (orthorhombic, monoclinic) with MX_n distorted complexes. In the literature, these distortions have usually been ascribed to Jahn-Teller (JT) effect, discussed on the basis of simple parametrized models, which assume that the JT theory can be transferred from cubic to lower symmetries, an assumption that is, in general, mistaken [2-5].

Our study takes a different approach, based on the vibronic coupling framework with a particular focus on the symmetry. A key concept in our work is the *parent phase* [3], whose symmetry and degeneracy are directly linked to the distortion undergone by the systems. If the ground state of the MX_n units in the parent phase is non-degenerate, thus excluding the JT effect [2-5], the mechanism of symmetry breaking is the pseudo Jahn-Teller (PJT) effect. Despite having similar names, the physics involved in each case is entirely different [3].

The results obtained for inorganic K_2CuF_4, Rb_2CuF_4, Na_2CuF_4, Na_3MnF_6 and the hybrid $(C_2H_5NH_3)_2CdCl_4{:}Cu^{2+}$ layered materials [2-5] show that their parent phases are tetragonally compressed. Thus, the ground state is *non-degenerate* and therefore the driven force is the PJT effect, which elongates one of the in-plane distances. Due to this *orthorhombic instability*, the response to pressure of these systems is highly anisotropic and can lead to switches of the main axes [4] or significant changes in the optical spectra [5].

Acknowledgments: The authors acknowledge financial support from Grant PGC2018-096955-B-C41 by MCIN/AEI/ 10.13039/501100011033 and by “ERDF A way of making Europe”, by the EU. I.S.M. acknowledges financial support from grant BDNS:589170

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KN-3: Determination of Endogenous Proteins in Individual Cells From an *In Vitro* Model by Elemental Mass Spectrometry

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Keywords: Metal-tagged antibodies, Laser ablation ICP-MS, Single cell ICP-MS, Bioimaging, Metal nanoclusters

Cell populations in biological systems are well-known for their heterogenous nature. Under the same physiological conditions and external stimuli, cells from the same line may show different biomolecule expression. For that reason, differences among cell populations can be difficult to elucidate unless they are studied cell by cell. In this context, there is a need to develop new analytical methodologies allowing for the quantitative determination of the content (endogenous metals and biomolecules) of individual cells.

Over the last few years, single cell (sc) ICP-MS has been employed for the analysis of the endogenous metal content of individual cells, the uptake of metallodrugs or the internalization of metallic nanoparticles. Moreover, if combined with immunocytochemistry, it is possible also to determine endogenous biomolecules within individual cells if labelled with metal tagged immunoprobes [1]. However, spatial information is lost with this sample introduction strategy. This could be overcome by sampling the cells using laser ablation (LA) coupled to ICP-MS.

In this work, sc-ICP-MS and LA-ICP-MS are investigated as complementary tools for a comprehensive study of specific proteins in individual cells from an *in vitro* model of retinal pigment epithelium (ARPE-19 cell line). On the one hand, sc-ICP-MS allows for the quantitative determination of proteins in single cells even at attogram level [2]. On the other hand, LA-ICP-MS allows the elucidation of the protein spatial distribution within cellular structures. The methodology employed for the study of specific proteins in ARPE-19 cells uses iridium nanoclusters (IrNCs) as the elemental label for ICP-MS detection. A case study for the determination of APOE and Claudin-1 proteins in individual ARPE-19 cells (control and subjected to a stress treatment with glucose) is presented.

Acknowledgments: This work was financially supported through projects PID2019-107838RB-I00/Agencia Estatal de Investigación (AEI)/10.13039/ 501100011033) in Spain and AYUD/2021/51289 - FICYT. P. Menero-Valdés acknowledges the FPU Grant with Ref. FPU19/00556 (Ministry of Education, Spain).

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KN-4: Effect of H_2S in Biogas Composition on the Production of H_2 by Sorption Enhanced Steam Reforming (SESR)

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Keywords: biogas, hydrogen, CO_2 capture, H_2S impurities, reforming.

Hydrogen is recognised as a promising clean fuel for the future. Recently, sorption enhanced steam reforming (SESR) has emerged as an intensification technology of conventional natural gas steam reforming (SR) that includes in situ CO_2 capture. However, the substitution of natural gas with renewable feedstock is still needed. With this purpose, biogas SESR is the topic of our research. The experiments were performed in a stainless steel fixed-bed reactor with a bed composed of a catalyst synthesized in the laboratory (1% Pd/20%Ni-20%Co hydrotalcite) and a solid sorbent for in situ CO_2 capture (commercial Artic dolomite, $CaMg(CO_3)_2$). The influence of biogas composition was evaluated in SESR and SR at 600 and 650 ºC, $S/CH_4 = 6$ mol/mol, and GHSV=1969 $mL_{CH4}/(g_{cat}\cdot h)$ for all the biogas compositions (50-95 CH_4 vol.%, CO_2 balance) and pure methane. The experiments showed that all the CO_2 supplied with the biogas is removed by the sorbent, independently of the biogas composition, and it does not affect the SESR process compared to pure methane. High H_2 purity (98.4 vol.%) and H_2 yield (91%) were obtained for all the compositions tested. During the experiments including H_2S in the composition of biogas, initially, a set of experiments varying the operating conditions were performed and then, the cyclic activity of the bed was evaluated in the more favorable conditions (600ºC, $S/CH_4 = 6$, and $GHSV_{CH4}$ of 1.8034 $L_{CH4}\ g_{cat}^{-1}\ h^{-1}$) for biogas (60/40 vol.% CH_4/CO_2) containing different concentrations of H_2S (150, 350, 500, and 1000 ppm). The results showed that H_2 yield, selectivity, CH_4 conversion, and gas composition for the lowest H_2S concentration were kept constant upon cycling, indicating the absence of deactivation of the catalyst for at least five consecutive cycles of SESR-regeneration. However, a slight decrease in those parameters can be observed from cycle number 5 for 350 ppm and cycle 4 for 500 and 1000 ppm. All the experimental results were compared with the equilibrium predictions obtained in AspenPlus using the Gibbs energy minimization approach.

Acknowledgments: the authors thank Franefoss Miljøkalk AS (Norway) for supplying Arctic dolomite and the financial support from the projects PID2020-119539RB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and PCTI, Ref. IDI/2021/000060 funded by Gobierno del Principado de Asturias. A. Capa acknowledges a fellowship awarded by the Spanish MICINN (FPI program, PRE2018-083634) and M.V. Gil acknowledges support from the Spanish Agencia Estatal de Investigación (AEI) through the Ramón y Cajal Grant RYC-2017-21937 funded by MCIN/AEI/ 10.13039/501100011033 and by "ESF Investing in your future".

KN-5: An Original Way to Synthesize (*Z*)-*β*-silylenamides by Silylium-Catalyzed Carbosilylation of Ynamides

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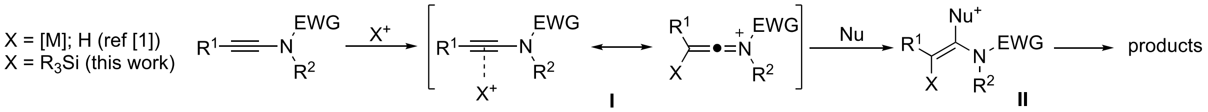
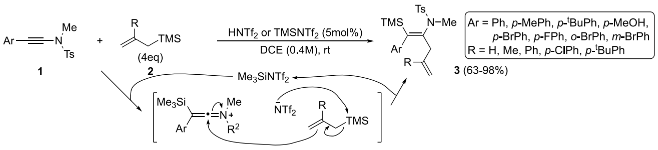
Keywords: Ynamides, Catalysis, Silylium Ion

Ynamides, have attracted substantial attention in the past two decades for their abundant chemical transformations,[1] and their tendency to be activated by carbophilic species such as transition metal complexes or Brønsted acids. On the other hand, the recent outbreak of silylium ion catalysis[2] has opened the possibility of using these reactive intermediates as carbophilic species able to activate unsaturated C-C bonds.[3] In this context, tosylynamides could be a good example of an electron-rich C-C triple bond system to be activated by silylium species; in particular their selective carbosilylation employing silylium ion as catalyst as here is described.



After preliminary studies employing different silylium ion sources, and the corresponding reaction optimization, we found that *N*-methyl *p*-tolylsulfonyl ynamides **1** can be selectively allylsilylated by treatment with different allylsilanes **2** in the presence of catalytic silylium ion to give *Z*-*β*-silyl enamides **3**. The reaction proceeds in mild conditions and good yields employing 5 mol% of either trimethylsilyl bistriflimide ($TMSNTf_2$) or bistriflimidic acid ($HNTf_2$) as silylium ion precursor. The regio- and stereoselective outcome of the reaction was unequivocally determined by X-ray analysis of selected products **3**.



In addition to the unprecedented use of silylium ion as carbophilic species for the activation of electron-rich triple C-C bonds, this reaction represents a direct metal-free entry to *β*-silylenamides, useful precursors for the synthesis of functionalized alkenes.[4]

Acknowledgments: AEI (PID2019–107469RB–I00/AEI/10.13039/501100011033)

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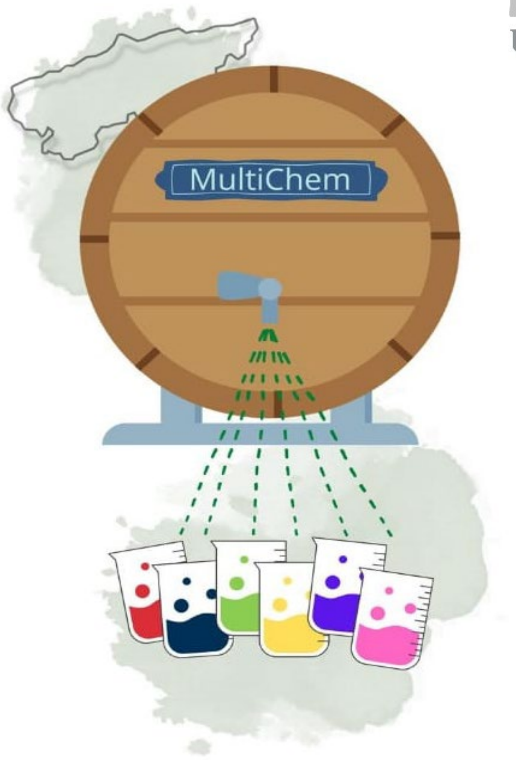

ORAL COMMUNICATIONS

OC-1: Signal Drift in Electrochemical, Aptamer-based (E-AB) Sensors: Enderstanding its Mechanism and Future Challenges

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Keywords: aptamers, continuous monitoring, electroanalysis, monolayers, voltammetry

Electrochemical, aptamer-based (E-AB) sensors are analytical platforms that support the continuous monitoring of molecular targets in vivo.[1] The architecture of E-AB sensors generally consists of three different elements: (1) nucleic acid aptamers self-assembled on the surface of gold electrodes via S-Au bonds that selectively bind the target molecule, (2) a redox reporter chemically attached to the terminal end of the aptamer, generally Methylene Blue, and (3) a blocking monolayer of short-chain alkylthios self-assembled on the electrode surface that prevents the interference of redox active molecules present in the sample (e.g., dissolved molecular oxygen). In the presence of target, aptamers undergo reversible, binding-induced conformational changes that modify the electron transfer of the redox reporter with the electrode surface, thus enabling the real-time and continuous monitoring of analyte concentrations. Although this new technology has the potential to change the landscape of continuous molecular monitoring, particularly for health monitoring applications, the rapid signal loss observed when E-AB sensors are deployed in vivo still limits their potential applications.[2] This contribution evaluates the main mechanisms of signal loss and describes some alternatives to overcome such loss including the electrochemical technique used for the interrogation, the nature of the blocking monolayer, or the electrode material.

Acknowledgments: National Institute of General Medical Sciences of the National Institutes of Health under the award number R01GM140143

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OC-2: Main Group Mechanochemistry: Challenges and Opportunities for a Sustainable Society

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Keywords: mechanochemistry, ball-milling, catalysis, solvent-free, main group elements

Traditionally, solution-based processes have dominated laboratory set-ups and industrial manufacturing protocols. However, the past decade has seen the renaissance of solid-state synthetic routes, driven by the need for more sustainable chemical processes. Within this context, mechanochemistry (i.e., chemical transformations initiated or sustained by mechanical force) has rapidly evolved from being a laboratory curiosity to a widely applicable synthetic technique that not only enables greener chemical transformations but offers exciting opportunities for the synthesis and screening of molecules and materials.

This seminar will focus on the recent developments in reactive mechanochemistry of main group compounds and materials. The novel application of mechanochemistry to the synthesis of different salen and salophen ligands followed by their complexation with photoluminescence Group 13 photoluminescence. This will be followed by an explanation about their utilization as catalyst for the mechanochemical chemoselective cycloadditions to readily accessible epoxide derivatives of with CO_2 and CS_2. Finally, a brief discussion on the challenges facing the broader adoption of mechanochemistry in industry, with focus on the upscaled synthesis of metal complexes and perovskites, temperature-control reactions and their future utilization of mechanochemistry for carbon capture and storage (CCS).

Acknowledgments: We would like to thank A*STAR AME IRG (A1783c0003 and A2083c0050), NTU for a start-up grant (M4080552) and MOE Tier 1 grants (RG 11/15 and RG 113/16) We would like also to thanks the support of Fundación para el Fomento en Asturias de la Investigación Científica Aplicada y la Tecnología (FICYT) through the Margarita Salas Senior Program (AYUD/2021/59709).

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OC-3: Impact of Chelate Cooperativity on the Supramolecular Structure of Self-Assembled Nanotubes

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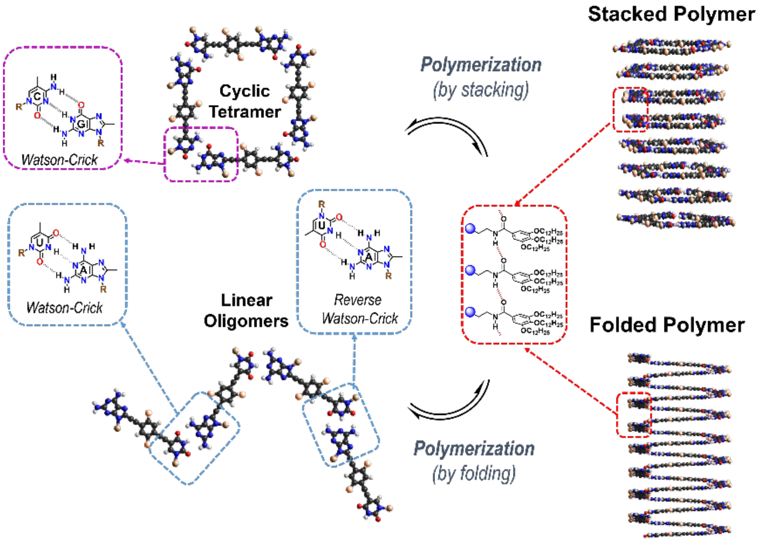
Keywords: Supramolecular, Nanotube, nucleobase, self-sorting

Inspired by the structure and performance of natural systems, chemists have developed numerous approaches to **self-assembled nanotubes**.[1] Diverse supramolecular strategies that can generate macrocycles that orderly ***stack*** on top of each other, or flexible linear oligomers that can ***fold*** into helical structures (i.e. foldamers) have been explored. In any case, for a monomer for which these two possible pathways are in principle available, it is difficult to predict the kind of tubular architecture generated. Herein, we study in detail the **self-assembly** of two almost identical molecules (**GC** and **AU**) having complementary nucleobases at the edges.[2] Whether these monomers undergo a **cyclization-stacking** or **folding-polymerization** process depends on the cooperativity shown towards the formation of a **Watson-Crick H-bond** between macrocycles.



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OC-4: Understanding Ruthenium-Prompted Amine Fixation: Deep Insight on Bonding Evolution Theory

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Keywords: DFT, Quantum Chemical Topology, Chemical Bonding, ammonia fixation.

The underlying interest on the obtention of N-derivatives on the chemical sphere has put the amine fixation on the spotlight, where the N−H bond breaking is carried out. However, due to the strength of this bond, this process represents a difficult task. Many possible reactions have been designed with the aim of overcoming the trouble[1]. Among the strategies proposed, the activation via metal-based complexes have seemed to be the most relevant. Notwithstanding the suitability, they are not trouble free as newly formed amides coordinate strongly coordinate to the metallic centre, yielding very stable Werner-type complexes.

In this sense, Milstein and co-workers[2] reported a series of Ru-based complexes bearing non-innocent PNP pincer ligands able to mediate the direct fixation of ammonia under soft reaction conditions, which was a milestone in the field. The metal-ligand mediated process follows a favourable electronic rearrangement that operate via aromatization-dearomatization of the pyridine scaffold within the pincer ligand[3]. Nonetheless, despite several advances, the electronic features that govern these processes are far from being completely understood.

In this context, original complex proposed by Milstein is taken as the model system to attain a further understanding on the factors that affect the performance of such systems at a molecular level. Thus, electron rearrangement is studied across the reaction pathway by means of Bond Evolution Theory (BET) elucidating the bond formation and breaking events[4]. On the basis of the results, we proposed rational ligand modifications to improve the kinetics and thermodynamics of the process, what allowed us to delve into the electronic behaviour of the system and will be able to lay the foundation for further improvements into this single-step reaction.

Acknowledgments:

The authors express their appreciation for the financial support from the Spanish MICINN under the project PGC2018-095953-B-I00 and “Fundación para el Fomento en Asturias de la Investigación Científica Aplicada y Tecnológica” under the grant IDI-2021-000054.

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OC-5: Optimizing the Process Variables for Microwave-Induced Synthesis of Iron Aerogels

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Keywords: microwave, sol-gel, transition metals, aerogels, electrochemistry.

Energy demand has risen steeply in recent decades, as well as the need to supply this energy in a sustainable way through its decarbonization using renewable energy resources. In this context, alternative clean energy fuels have gained importance to overcome the shortage of conventional energy sources without contributing to global warming. Electrochemical devices to generate and store clean and sustainable energy, such as hydrogen fuel cells, have become very attractive [1]. In fuel cells, hydrogen and air can be used to generate electricity through electrochemical reactions, i.e. by the reduction of oxygen and the oxidation of hydrogen (ORR and HOR, respectively), being the ORR the sluggish reaction. In order to have an efficient performance in these devices, it is mandatory to use electrocatalysts, being platinum the most commonly used, which is expensive and scarce [2]. Therefore, to develop efficient and sustainable devices, it is essential to develop new materials with lower cost, higher availability, and high electroactivity.

Transition metal aerogels (TMA) are presented as potential electrocatalysts to replace platinum. In this study, the microwave-assisted sol-gel reaction has been optimized for the first time to obtain iron aerogels. This methodology allows obtaining aerogels with highly porous three-dimensional structures that provide a high number of active centers via a fast and clean process. Iron aerogels have been characterized by different techniques to determine their physicochemical properties. SEM, XPS and XRD were employed to analyze their morphology, surface elemental composition, and crystallinity, respectively. The characterization results demonstrate that the morphology of the TMAs can be successfully controlled by modifying the synthesis conditions. Moreover, the electroactivity of these materials against ORR has been preliminarily tested using a rotating ring-disk electrode through different electrochemical techniques: cyclic voltammetry (CV), linear voltammetry (LSV), and electrical impedance spectroscopy (EIS). The electrochemical results suggest that certain three-dimensional structures make iron aerogels electroactive and susceptible to being used in fuel cells.

Acknowledgments:

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OC-6: Determination of Methylmercury and Inorganic Mercury in Human Hair Samples of Individuals From Colombia by Double Spiking Isotope Dilution and GC-ICP-MS

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Keywords: mercury, methylmercury, inorganic mercury, isotope dilution, GC-ICP-MS

Mercury (Hg) is a toxic substance of major public interest due to its increasing emissions to the atmosphere by both natural and anthropogenic sources, such as the amalgamation from artisanal small-scale gold mining (ASGM). In the course of ASGM activities, not only harmful vapors are released to the atmosphere, but Hg residues enter to aquatic ecosystems, where part of them are transformed into methylmercury (MeHg). This MeHg is biomagnified through the trophic chain, being fish consumption the main route of Hg exposure for humans [1]. Colombia stands out as one of the world's leading gold-producing countries, as a great part of its rural population is involved in mining-related tasks. Hg uses in artisanal gold mining are well widespread in Colombia, thus the country is the most mercury polluting per capita. Hg species-specific determination in indigenous population samples provides a general exposure view, either from Hg burning vapors or from consumption of contaminated fish. Most studies of human exposure to Hg are focused on the determination of total mercury (THg) in different biological biomarkers such as blood, hair, or urine. However, the determination of inorganic mercury (Hg(II)) and methylmercury (MeHg) along with THg can provide useful information on the exposure sources [2]. In this work, MeHg, Hg(II) and THg concentrations were determined in 96 human hair samples of individuals, mostly non-directly occupied in ASGM tasks, from six different Colombian regions: five Andean regions (Nariño, Chocó, Antioquia, Bolivar and Sucre) and one Amazonian region (Vaupes). The determination of Hg species was done by gas chromatography coupled to inductive plasma mass spectrometry (GC-ICP-MS). Sample quantification was carried out by isotope dilution analysis with a double tracer to obtain accurate and precise results and to correct for interconversion between species during the sample preparation procedure [3].

Acknowledgments: Financial support from the Spanish Ministry of Science and Innovation through Project PGC2018–097961-B-I00 is acknowledged. Principality of Asturias, Spain, for their financial support through the Severo Ochoa scholarship (BP19-131). The authors would also like to acknowledge the Spanish National Research Council (CSIC) through project I-COOP+2021-COOPA20490 and the Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo (CYTED), for financing the MercuRed Network (420RT0007).

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OC-7: Development of a Paste Extruder System and Production of Ni-Electrodes by DIW for Water Splitting

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Keywords: Additive Manufacturing, Direct Ink Writing, Water Splitting, Ni.

Among the AM technologies based on material extrusion, the direct ink writing (DIW) technique stands out for its simplicity and versatility in terms of the wide palette of compatible materials. This technique consists of the extrusion of a pseudoplastic fluid filament designed with a specific rheology that ensures smooth flow during printing and stiffness of the printed object.

The aim of this study was to design and build a low-cost, lightweight printer head which can be coupled with a commercial Fused Deposition Modelling (FDM) printer, thus enabling DIW printing modes. To size the structure of the extruder system, a static stress simulation was carried out using finite element analysis. The structural parts that make the structure up were printed in PLA by an FDM printer. The paste extruder system developed allows the printing of pre-loaded material in a 3 mL syringe using different nozzles (0.25-1 mm) being able to apply an extrusion force of more than 200 N.

Finally, the DIW additive manufacturing technology was applied to the printing of active electrodes in the OER and HER water splitting reactions in alkaline conditions. As a base material, a solution of 25 wt.% Pluronic F-127 as carrier of 79 wt.% Nickel powder (3-7 µm) was used. After printing, the green parts were sintered at 900°C, 1h, in inert atmosphere, then Ni and Fe were electrodeposited on the electrode surface forming double layered hydroxides (LDHs), which significantly improves the activity of the workpiece.

Acknowledgments: P. Rodriguez acknowledges to Spanish Research Agency for its grant JAE INTRO ICU (JAEICU21-INCAR-40). V.G. Rocha would like to thank the Spanish Government (Ramon y Cajal fellowship, RYC2018–024404-I) and the support from the Spanish Research Agency AEI/PID2019–104028RB-100.

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OC-8: Albumin-Based Nanomaterials: a Novel Treatment for Triple-Negative Breast Cancer

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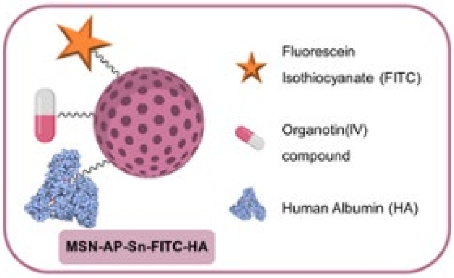
Keywords: *triple negative breast cancer, organotin compounds, albumin, theranostic nanosilicas*

Breast cancer is the most common cancer in women worldwide, with an incidence of 11.7% and a mortality rate of 6.9%, which leads to approximately 685,000 deaths per year [1]. Triple negative breast cancer (TNBC), accounts for 15-20% of breast cancers and presents serious difficulties in its treatment due to the absence of the three most common receptors (HER2, estrogen and progesterone) in breast cancer, which makes treatment with traditional drugs ineffective [2]. Therefore, the search for innovative treatments for TNBC is an emerging challenge for oncology researchers.

COMET-NANO research group is focuses on the use of nanomaterials based on silicon oxides as starting vehicles for different biomedical applications as they are an interesting option due to their excellent physico-chemical properties, such as wide functionalization possibilities, high loading capacity and biocompatibility, which makes them suitable for this treatment [3]. Therefore, this work focuses on the preparation and modification of mesoporous silica nanoparticles (MSNs) with metallodrugs for their potential use as a theranostic material against TNBC (Figure 1). Thus, MSNs have been functionalized with an organotin(IV) compound as cytotoxic agent, fluorescein isothiocyanate (FITC) to provide the material with diagnostic capacity and human albumin (HA) at different concentrations as *target* molecule.

This novel nanosystem was characterized by different physico-chemical techniques to verify its correct functionalization. Subsequently, its cytotoxic potential was evaluated *in vitro* against the TNBC cell line (MDA-MB-231), showing a dose-dependent activity of the materials studied. The MSN-AP-Sn-FITC-HA material has shown promising therapeutic properties as a theranostic agent against triple negative breast *cancer in vitro*, paving the way for future *in vivo* studies.



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OC-9: Discrimination of TNT and its Metabolites in the Environment Using Voltammetric Sensors, Modified With Molecularly Imprinted Polymers

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Keywords: Voltammetry, molecularly imprinted polymers (MIPs), TNT, electronic tongue (ET).

Given their low degradation rate and carcinogenic nature [1], TNT and its possible metabolites [2] tend to accumulate in sediments and groundwater. Thus, the need for cheap, portable, and easy-to-use devices that allow a quick determination of this pollutant in water samples becomes crucial for the environmental control of storage locations, post-war and mining areas where this explosive may have been used.

Instead of following a classical approach based on the designing of specific sensors for each one of the species, we propose an alternative methodology profiting from the cross-sensitivity of an array of non-specific voltammetric sensors modified with molecularly imprinted polymers (MIPs) in a multiplex analysis system. Using chemometric tools (e.g., Principal Component Analysis, PCA. and clustering algorithms, [3]) we are able to extract useful analytical information from the large amount of resulting experimental data so that a qualitative and quantitative analysis of the presence of these analytes in water samples is feasible.

After studying 15 TNT metabolites, our results show the possibility to detect and identify most of them (practically 85%) in water samples by means of a simple array of four sensors: two modified with specific MIPs for two target analytes, 4-Nitrotoluene and 2,4-Dinitrophenol; and two non-specific sensors, the bare electrode (Graphite epoxy electrode) and one modified with non-imprinted polymer (NIP). This opens the door to the designing of an electronic tongue (ET) capable of determining contamination of groundwater by TNT relaying on a cheap, as it only requires few modified sensors for its construction; portable, as all measuring equipment can be put in a briefcase; and easy-to-use, as no pretreatment of the samples is needed.

Acknowledgments: The authors acknowledge the support of the Spanish Ministry 623 of Science and Innovation (project PID2019-107102RB-C21/ 624 AEI/10.13039/501100011033).

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OC-10: Scalable Divergent Synthesis of Diterpenoid Pyrones

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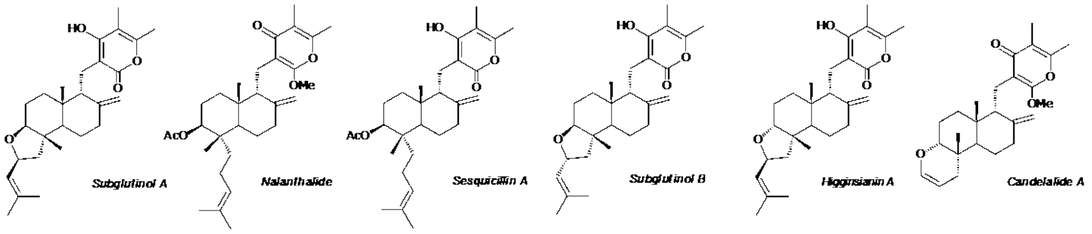
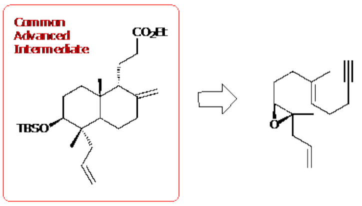
Keywords: cationic cyclization, diterpenoid pyrones, natural products, total synthesis

In the last years, several diterpenoid pyrones have been isolated from microorganisms. Many of these natural products exhibit a wide variety of biological properties. These natural products consist of a decalin skeleton connected with a fully substituted α- or γ- pyrone ring involving five asymmetric carbon centers and an exocyclic alkene. So, due to this unique structure and the interesting biological properties, the development of efficient and flexible synthetic methods is desirable from the viewpoint of medicinal chemistry.[1] In recent years, we have been involved in the development of new biomimetic cationic cyclization reactions for the stereoselective construction of complex scaffolds from simple starting materials.[2] In this context, we have designed an innovative approach to the synthesis of several diterpenoid pyrone-containing natural products from a common advanced intermediate. Herein, we present our studies on the synthesis of this common intermediate and our progress on the total synthesis of the final natural products.





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OC-11: Perylene-Based Chromonic Self-Assemblies for the Preparation of Hierarchically Porous Silica and Carbon Nanofibers

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Keywords: Perylene bisimides, chromonic liquid crystals, silica, carbon, nanofibers

Chromonic liquid crystals are lyotropic mesophases formed by planar polyaromatic compounds functionalized with hydrophilic groups at the periphery, which impart to these molecules solubility and capacity to self-assemble in water forming columnar aggregates in which the hydrophobic polyaromatic cores stack via π-stacking. At high concentrations, such columnar self-assemblies gain orientational and/or positional order forming chromonic mesophases, which can be exploited to prepare advanced nanomaterials. Herein, we describe the synthesis of 5 PEGylated water-soluble perylene bisimides (molecules formed by 5 fused benzene rings functionalized with two oligoethylene glycol at each side through an imide bond), and discuss their aggregation behaviour and the formation of nematic and hexagonal chromonic mesophases in function of the length of the oligoethylene glycol side chains, through spectrophotometric techniques, polarized optical microscopy and SAXS. Furthermore, the formed perylene-based chromonic mesophases were used as templates for preparing nanostructured silica-perylene composites which yielded microporous silica fibers upon calcination [1]. Moreover, we also describe the preparation of nanostructured composite silica-perylene fibers using a cationic perylene bisimide as template and the obtention of hierarchically porous N-doped carbon nanofibers through carbonization and etching. Remarkably, the obtained carbon nanofibers showed high surface area, heteroatom (N and O) doping and wettability, which gives them potential applications as materials for electrodes for super and pseudocapacitors [2]. These results show the potential of chromonic mesophases as templates for the preparation of fibrillar porous nanomaterials with controlled properties and applications in many fields.

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OC-12: Development of New pH-Responsive Delivery Systems

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Keywords: diruthenium, delivery systems, pH-responsive

Paddlewheel diruthenium complexes have been widely studied in the last decades, mainly from a fundamental point of view. Nonetheless, we are currently looking for novel applications of these compounds. They consist on a bimetallic unit supported by four bridging ligands. We have developed a carboxylate pH-responsive delivery system that includes three formamidinate ligands and a carboxylate as the fourth ligand (Figure 1a). The carboxylates were three different phytohormones, called auxins (Figure 1b), whose biological activities can be determined *in vivo* employing transgenic *Arabidopsis thaliana* plants. The plants were treated with the auxin-containing complexes, measuring the auxin activity in different pH conditions to estimate the release of the auxins. We have qualitatively demonstrated that the carboxylate ligand (auxin) is released in a slightly acidic medium (pH = 6.5-7.0). Nevertheless, the complexes are practically inert under normal physiological pH conditions (pH~7.4)[1]. This pH-responsive release ability is of great interest for the development of new drug delivery systems for cancer chemotherapy since solid tumours suffer extracellular acidosis (pH = 6.4-7.0). It is expected that our system can be employed as anticancer drug delivery system, where the drug is coordinated through a carboxylate group in order to be released exclusively in the tumour surroundings. We have studied the effect of the formamidinate ligands on the release of the phytohormones from the diruthenium complexes. For this aim, new pH-responsive delivery systems with different formamidinate ligands have been synthesized (Figure 1c). The kinetics of the auxins release have been quantitatively analyzed in order to develop the most suitable candidate for cancer chemotherapy in the near future.

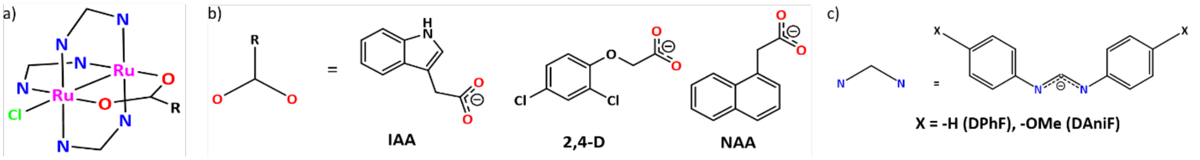

Figure 1. a) pH-responsive delivery systems; b) auxins employed: indole-3-acetate (IAA), 2,4-dichlorophenoxyacetate (2,4-D), and 1-naphthaleneacetate (NAA); c) formamidinate ligands: N,N´-diphenylformamidinate (DPhF) or N,N’-bis(p-methoxy)phenylformamidinate (DAniF).

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OC-13: MD and DFT Combined Simulations

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One of the most demanding challenges confronting the construction of commercial nuclear fusion reactors is the development of new advanced materials that are more resistant in extreme operating conditions. Tungsten is postulated as one of the most promising candidates as plasma facing material (PFM) in future fusion reactors, as it satisfices most of the highly demanding requirements. However, previous works indicate that W also has major drawbacks, being the deleterious tendency to easily retain light species (LIA, light interatomic atoms) the main one, which causes, among other fatal effects, the formation of bubbles, cracks, and exfoliation of the material. Recently, numerous publications have reported that nanostructured materials are, under certain circumstances, more resistant to radiation, mainly due to the high density of grain boundaries (GB)[1]. This imply that the overpressurization of the bubbles can be delayed, thus increasing the limit of radiation damage that the material can accepts without seriously compromising its performance. The best situation would be if the GBs not only behave as defect sinks, but also as effective channels diffusion, promoting the outgassing of defects.

For that purpose, we'll carry out a methodology in which MD calculations will be combined with DFT ones. Due to the high computational cost of DFT calculations in this type of configurations, previously relaxing the system with MD will allow us to start from initial configurations closer to equilibrium and therefore save DFT computation time, in addition to testing the MD interatomic potential. These calculations will focus on studying energetic and structural analysis, in addition to the migration barriers of the different defects to and on the GB.

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OC-14: Development of Carbon Materials for Na-ion Capacitors

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Keywords: hybrid ion capacitor, sodium, porous carbon, S-doped, energy storage.

S-doped carbon sponges have been synthesized by an eco-friendly approach based on a salt-templating strategy followed by a facile S-doping process. Gluconic acid has been chosen as sustainable precursor, sodium carbonate as low toxicity and water-removable template, and sulfur as environmentally benign and earth-abundant S-dopant. These carbon sponges are characterized by a 3D structure composed of thin interconnected carbon walls with a highly disordered structure, a dilated interlayer spacing (> 0.36 nm) and a high content of electrochemically active covalent sulfur (up to 13% by weight, mainly as thiophene groups). As a result, they provide a sodium storage capacity of up to 524 mAh g^{-1} at 0.1 A g^{-1} and 161 mAh g^{-1} at 10 A g^{-1}.

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OC-15: Graphene Aerogels as Nanomaterials for Electrochemical Detection of Biomarkers

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Keywords: Aerogel, graphene, nanomaterials, electrochemistry, sensors.

Electrochemistry is a promising application for graphene-based nanomaterials due to their high purity, great chemical stability, and exceptional electrical conductivity. Among the possible electrochemical devices, the field of sensors is of special interest due to the high level of sensitivity required and the possibility of miniaturizing devices. The use of graphene-aerogels reduces the stacking of graphene sheets, forming three-dimensional structures and increasing the number of available active sites [1]. Therefore, in this work, graphene aerogels are obtained and tested as potential electrode materials in electrochemical sensors for glucose detection.

Carbon gels (CG) and graphene aerogels (GA) were synthesized by microwave-assisted sol-gel synthesis [2]. Resorcinol, formaldehyde, distilled water or a dispersion of graphene oxide were used as reagents. The sol-gel reaction was performed at 85°C for 3 hours. After the synthesis, the materials were dried in an oven at 85ºC until constant weight (CG) or in a lyophilizer after freezing (GA). The organic dried materials were carbonized and activated in a tubular furnace, and then, doped with nickel by incipient wetness impregnation with nickel acetate (III) with a subsequent reduction process at 600 ºC for 6 h. The synthesized materials were characterized in terms of their chemistry, microstructure, porosity, and electrical conductivity. Finally, all aerogels were electrochemically tested.

The materials obtained have a percentage of porosity between 70% (CG) and 98% (GA) and the electrical conductivity of GA is ten times higher than that of GC [3]. Therefore, GA has high conductivity and porosity, two characteristics that are difficult to achieve simultaneously. The XRD technique highlights that after the reduction treatment, nickel carbide is obtained, which is essential in the glucose electrooxidation process. The GA doped with Ni provides the highest anode peak intensity in the presence of glucose ($I_{p,a}$ 0.78 mA at 0.52 V), suggesting the interest of these materials for developing novel and effective materials to be used as biomarkers.

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OC-16: Compositional Similarities and Differences Between North West Africa (NWA) 2975, 10628 and 1950 Martian Shergottites

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Keywords: Martian Shergottites, meteorite, micro-Raman spectroscopy, XRF.

Understanding Mars's historical habitability is of growing scientific interest, and it has become feasible thanks to the information provided by meteorites and from data retrieved on Mars during mission exploration activities. Using this data, we have been able to classify the different types of samples according to their chemical compositions and alteration processes. As such, we are able to understand the typology of atmospheric processes and hydrous activity taking place in the Martian crust, as well as, both terrestrial and shock alterations [1]. In this case, three Martian shergottite meteorites (NWA 2975, 10628 and 1950) were considered, and were analysed using non-destructive analytical techniques (micro-Raman spectroscopy and micro-XRF imaging), with the aim of identifying their geochemical similarities and differences following a methodology described elsewhere [2]. The major minerals detected in the NWA 2975 specimen were pyroxenes and plagioclases. Furthermore, other minerals such as merrillite, pyrrhotite, ilmenite, apatite, mackinawite and coesite were also found. The NWA 10628 meteorite was mainly formed by pyroxenes and small crystals of plagioclase, whereas the secondary phases were whitlockite, fayalite, gypsum, anhydrite, pyrite, marcasite, hematite, whilockite, ilmenite, magnetite, goethite and calcite. Finally, the matrix of the NWA 1950 sample was mainly formed by olivine and pyroxenes, while magnesite, hematite, ilmenite, anatase, merrillite, chromite, acanthite and franklinite were detected as minor mineral phases. As a conclusion, it could be said that the analysis carried out show great similarities in the composition of the main matrix, while the secondary phases differ mostly because of the alterations (shock during ejection from Mars and entry to Earth atmosphere, and terrestrial weathering) produced within them.

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OC-17: TiO_2/SnO_2 – Silver Clusters Hybrid Nanomaterials for Catalytic Photodegradation of Micropollutants

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Keywords: Micropollutant, semiconductor, atomic quantum cluster, photocatalysis, photodegradation

Micropollutants consist of many natural and anthropogenic substances, present in trace concentrations, mainly in wastewater. These pollutants suppose a risk to health and the environment and are difficult to eliminate by conventional treatments[1].

Photodegradation using classic photocatalysts, such as TiO_2, have the drawback that they only absorb in the UV region and have very low efficiencies due to rapid electron-hole recombination. However, the addition of atomic quantum clusters (AQCs) has proved capable of modifying TiO_2 bandgap, resulting in enhanced light absorption and a reduction effect on the recombination rate of electron-hole pairs[2].

In this work, SnO_2/TiO_2 hybrid nanomaterials have been synthesized by the sol-gel method and characterized for later use in photocatalytic reactions as substrates of clusters. The clusters deposition method was incipient wetness impregnation. Then, they were studied by UV-Vis spectroscopy and diffuse reflectance spectroscopy to check how the deposition process improves the optical properties of the materials, increasing visible light absorption through the appearance of midgaps, which make these nanomaterials very interesting for photocatalytic reactions[2].

The photocatalytic activity of these hybrid nanomaterials has been studied by photodegrading methylene blue in water using a solar simulator. The results confirm the improvement in photocatalytic efficiency, achieved thanks to the deposition of clusters. In addition, different parameters relevant to photocatalysis were optimized, such as the deposition of AQCs, the catalyst concentration, or the shelf-life of the catalyst.

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OC-18: Development of On-Site Sensors for Quality Control in Agri-Food

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Keywords: near infrared spectroscopy, chemometrics, non-destructive methods, handheld, real time analysis

With the increase in food safety and quality control, the demand for food analysis has grown considerably, and the development of rapid, non-destructive methodologies has aroused much interest in the industry, both for the quantification of nutritional values and for the identification of pathogens and contaminants.

Portable Near Infrared Spectrometers (NIRS) are cheap and easy to use devices, that can be implemented for on-site quality and security control in food [1]. However, for the establishment of NIRS technology in the production line or in the analytical laboratory, it is necessary to develop robust calibrations to obtain qualitative and quantitative results with adequate precision for each parameter and minimizing errors [2].

This work will present results of different studies introducing the NIRS methodology, such as the quantification of macronutrients in pasteurized breast milk samples [3] or the detection of fraud in olive oil.

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OC-19: “Vermellogens” and the Development of CB[8]-Based Supramolecular Switches Using pH-Responsive and non-toxic Viologen Analogues

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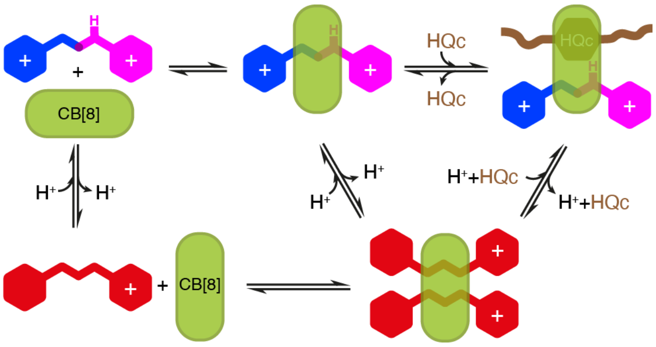
Keywords: Supramolecular chemistry, cucurbituril, host-guest chemistry.

A supramolecular switch is defined as a molecular device composed of two or more self-assembled units, whose association can be transiently promoted or disrupted by the application of an external stimuli,such as light, electrical potential, or chemical effectors [1]. Within the context of macrocyclic host−guest chemistry, the conjunction of the curcurbit[*n*]uril family of hosts, and viologens as guests (salts derived from the dialkylation of 4,4-bipyridine), is a paradigmatic example of supramolecular switches.

We present herein the “vermellogens” [2], a new class of pH-responsive viologen analogues. Furthermore, the parent *N*,*N*′-dimethylated “vermellogen”, an analogue of the herbicide paraquat and used herein as a representative model of the series, showed anion-recognition abilities, non-reversible electrochemical behavior, and non-toxicity of the modified bis-pyridinium core. The host−guest chemistry with the CB[7,8] macrocyclic receptors has been extensively studied experimentally and by DFT-D methods, showing a parallel behavior to that previously described for the herbicide but, crucially, swapping the well-known redox reactive capabilities of the viologen-based inclusion complexes by acid−base supramolecular responsiveness.



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OC-20: The Enhancing Effect of Iron on the Activity of Ni and Ni/Fe Graphene-Based Catalysts for the Electrolysis of Water

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Keywords: water splitting, oxygen evolution reaction, nickel catalyst, iron impurities, KOH purification

Water splitting is a key reaction for the clean production of hydrogen as sustainable fuel that consists of two half reactions, namely, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), being OER the bottleneck of this process. The state-of-the-art electrocatalysts for this reaction are based on noble metals (Ru or Ir complexes). However, high cost and scarcity of precious electrocatalysts prohibit large-scale application. Thus, it is essential to explore low-cost, earth-abundant, environmentally friendly, efficient and stable materials. In particular, Ni-based composites are potential substitutes for noble metals for its abundance and electrochemical efficiency.

In this sense, several studies have focused on investigating the activation mechanism of this metal in the OER. These previous studies showed that iron impurities present in the commercial KOH (reagent grade, 90%, flakes, Sigma Aldrich) used as electrolyte significantly alter the nickel catalysts activity [2,3]. Under these premises, water-based nickel lactate as precursor is combined with an aqueous suspension of graphene oxide to freeze-cast hierarchical porous structures (aerogels) that are then thermally reduced.

In this work, the electrochemical behaviour of these materials is studied for the OER reaction in basic medium containing iron impurities or purified [1], observing as a result differences that indicate an important role of iron in catalysis. To complete this work, (Ni/Fe)-based graphene-casted catalysts (different ratios of metal) are also prepared to study the activity of materials with iron in their composition. An improvement in activity was found by increasing the iron concentration when samples were tested in the purified electrolyte. The same trend was found using electrolyte with Fe impurities but the current densities obtained were higher.

This shows that the Fe present in the electrolyte also influences the activity of samples that have Fe in their composition.

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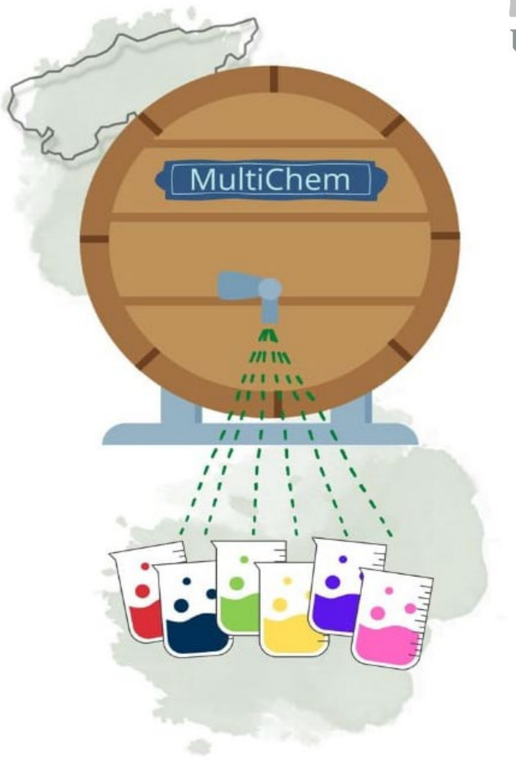

FLASH PRESENTATIONS

FP-1: Prostate Cancer Diagnosis by PSA Detection Using New Electrochemical Aptasensors

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Keywords: PSA, aptamers, prostate cancer, diagnosis, biosensors.

Prostate cancer, the most common men´s cancer, presents one of the highest mortality rates. Early diagnosis of this disease is based on the determination of prostate specific antigen concentration in serum. Nowadays, an unambiguous threshold PSA value which allows to distinguish between healthy and sick patients is still unknown[1]. As a consequence, patients with PSA values in the grey zone (4-10 ng/mL) are subjected to a prostate tissue biopsy in order to confirm a diagnosis that is often negative[2], being described up to 20% of false negatives. This explains the need for more specific biomarkers.

Protein glycosylation is a post-translational modification that is altered in case of cancer. In particular, there are several studies that relate changes in the glycan composition of PSA to malignant transformations and prostate tumor progression. Detection of aberrant PSA glycosylation might be more specific than the total PSA content. Our group has recently described the first aptamer with binary recognition to a glycoprotein, in this case PSA. It interacts not only with the sugar structure, but also with the amino acids surrounding the glycosylation site, which allows PSA to be distinguished from other glycoproteins with a similar glycan structure[3]. The PSA fraction reactive to this aptamer shows better discrimination between prostate cancer patients and people with benign prostate diseases[4].

Thus motivated, we search for the integration of this aptamer in an electrochemical aptasensor amenable to clinical laboratories. To this aim, we have designed self-reporting strategies comprising the formation of a mixed self-assembled monolayer on gold electrodes that contains the aptamer alone or hybridized to the complementary strand. One of the strands has been tagged with methylene blue as a redox probe. In this work we reported on the characteristics of those approaches and the advantages and disadvantages of using each of them. The ultimate goal is to obtain a reagentless easy-to-operate aptasensor to be implemented in clinical laboratories for massive screening of prostate cancer.

Acknowledgments: The work has been financially supported by Spanish Government (project PID2021-123183OB-I00).

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FP-2: Hydrogels-Based Systems for the Controlled Release of Therapeutic Agents: an Innovative Treatment for Osteoarthritis

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Keywords: Osteoarthritis, Silk fibroin hydrogels, Exosomes

Abstract: Osteoarthritis is a degenerative disease that affects the bones, joints and ligaments, resulting in a degradation of joint cartilage over time. This causes joint pain, inflammation stiffness, decreased mobility, and increased joint destruction. On average, more than 70% of the population over the age of 50 suffers from this disease. Nowadays, the treatment for osteoarthritis is symptomatic, since cartilage cannot be easily regenerated. Most common medications are non-steroidal anti-inflammatory drugs (NSAIDs) or painkillers that help to alleviate the pain that arises from this disease, but in the long term, they can cause ulcers and liver damage.

However, using exosomes from mesenchymal cells has demonstrated in the last years the potential to regenerate cartilage, becoming a powerful tool as a treatment for osteoarthritis. Though the direct exposition to exosomes may have undesired side effects, their slow release would induce the positive effects, without the undesired ones. According to this, the main aim of this work is to develop encapsulation systems for exosomes using hydrogels. A hydrogel is a network of water-rich 3D polymers formed by physical or chemical crosslinking of polymers, which can be used as a support system for other molecules or structures.

In this work, we develop protein-based hydrogels using different procedures. The final material is characterized using transmission electron microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), solid nuclear magnetic resonance (NMR), UV-Vis spectroscopy and differential scanning calorimetry (DSC). Exosomes-loaded hydrogels will be also characterized using the same techniques, and the load and release capacity evaluated by spectroscopic techniques.

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FP-3: Second Principles Density Functional Theory Models: a Procedure to Obtain their Tight-Binding Parameters Automatically

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Keywords: second-principles calculations, first-principles calculations, electronic degrees of freedom, tight-binding parametrization, $SrTiO_3$.

First-principles calculations allow to compute the energy and properties of a compound from essential information about its structure and composition. However, such simulations at operating conditions (finite temperature or electric fields) remain almost limited by computational resources to very small length scales (a few hundreds of atoms per cell) and timescales (a few picoseconds). A practical way to overcome these limitations is to work with effective atomistic models, integrating out the electronic degrees of freedom and providing a simple parametric description of the Born-Oppenheimer energy surface in terms of structural degrees of freedom. To reintroduce explicitly the treatment of the meaningful electronic degrees of freedom, a method has been proposed in the form of a tight-binding model [1].

This tight binding approach is based on the Taylor expansion of the DFT energy around a reference electronic density. The deformation density with respect this reference, as well as the hamiltonian matrix elements, is expressed in a basis of Wannier functions. Only the relevant electrons to the problem can be retained in the description, reducing by orders of magnitude the computational cost. This gain in efficiency would come at the cost of finding the right parameters in the tight binding hamiltonian matrix elements, that would reproduce as close as possible the first-principles calculations.

Here we propose a method implemented in python, the MODELMAKER code, for the automatic parametrization of such tight binding hamiltonian. The starting point is made of first-principles calculations (from the SIESTA code [2]) in training sets with a small number of atoms in the unit cell. Since there is not input coming from the experiment, our method retains full predictive power, and that is why it is coined as second-principles simulations. Both electron-lattice coupling and electron-electron interactions are included in the parametrization of the electronic model. The obtained parameters are validated comparing the band structures computed from first and second-principles in configurations that are not included in the training set. This methodology has been applied to a paradigmatic functional oxide such as $SrTiO_3$.

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FP-4: Effect of Landfill Leachate Age on Ultrafiltration Performance

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Keywords: Age; Fouling; Landfill leachate; Modelling; Ultrafiltration

The need for efficient management of leachate generated in urban landfills is steadily increasing [1]. To this end, membrane separation technology is considered a promising treatment. However, it has the drawback of membrane fouling, which can drastically reduce the flow of permeate generated [2]. In order to be able to design efficient operation and cleaning protocols, it is critical to have an in-depth understanding of the nature and formation mechanisms of fouling. Unfortunately, it is impossible to establish a generalized treatment, since these are extremely variable streams, with the age of the leachate being a critical factor in this variability [3]. Therefore, the objective of this work was to study the effect of the age of the leachate on the mechanisms of membrane fouling.

The ultrafiltration experiments were performed at 70ºC and 1.6 bar with a 150 kDa membrane. The aging of the leachate had a positive effect on its ultrafiltration, presenting a final permeability two times higher compared to the young leachate. This difference was due to the higher reversible fouling generated during the filtration of the young leachate, presumably due to its higher organic load. In any case, most of the loss of permeability was due to reversible fouling, and presenting similar values regardless of the age of the leachate. Fouling modeling showed that, in both types of leachate, the main mechanism is cake formation.

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FP-5: Effect of Interleukin 4 loaded Citrate Coated Iron Oxide Nanoparticles on Macrophage Polarization for Bone Regeneration

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Keywords: iron oxide, nanoparticles, interleukin 4, macrophage polarization

Macrophages are a cell type with a critical function in the regulation of bone healing, able to instruct bone regeneration upon biomaterials implantation. During the regeneration process, macrophages undergo a phenotypic switch from a pro-inflammatory type (M1) to an anti-inflammatory profile (M2) able to promote osteogenesis. This process called polarization can be induced by cytokines as interleukin 4 (IL-4), apart from other factors. Magnetic iron oxide nanoparticles (NPs) have been widely studied as magnetic contrast agents, hyperthermia agents and magnetic vectors. These NPs allow the uploading of therapeutic molecules (IL-4) over the shell for inducing macrophage polarization towards M2 [1].

In this work, two different systems consisting of single-core and multi-core citrate coated iron oxide NPs, hereafter SC and MC respectively, loaded with IL-4 were prepared. SC and MC were characterized by electron transmission micrography (TEM), infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). The loading efficiency of IL-4 on the NPs was determined by Micro BCA™ Protein Assay Kit. The obtained NPs presented a TEM diameter of 11 nm for SC and 146 nm for MC, with a loading efficiency for IL-4 of 93% for SC and 81% for MC.

The IL-4 loaded NPs were internalized by M1 macrophages through passive transfection and magnetotransfection. Their effect on polarization towards M2 phenotype was studied through the analysis of the secretion of pro-inflammatory (INF-γ, TNF-α) and anti-inflammatory (IL-13, M-CSF, IL-10, IL-17/IL-17A) cytokines. With passive transfection, both SC and MC showed anti-inflammatory response, which was greater in the case of SC. In the case of magnetotransfection, SC triggered an anti-inflammatory response, while MC provoked a strong pro-inflammatory response, which can be due to the formation of large aggregates that leads cells to a stressed state.

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FP-6: Modelling Optical Phenomena via Real-Time TD-DFT using Second-Principles: Measuring the Effect of Electron-Hole Interactions

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Keywords: second-principles, electron-phonon correction, electron-electron correction, real-time TD-DFT, localized Wannier-function.

Solid state spectroscopy is a fundamental topic in the development of new technological applications as modern electronic devices or more efficient energy conversion and storage strategies. The optical spectra obtained from experimental measurements are influenced by the presence of impurities, lattice distortions (phonons) or electron-scattering, and the results can be strongly dependent on the boundary conditions like strain or temperature. *Ab-initio* calculations can be useful to interpret and understand the results as these factors can interplay with electronic structure in non-trivial ways. However, these simulations will often require tens of thousands of atoms to obtain a detailed sampling of atomic movement/impurity localization, and need a detailed description of electron-lattice coupling and electron correlation.

Therefore, it would be desirable to go beyond the capabilities of standard first-principles methods. This fact motivates the development of a new family of methods, known as Second Principles (SP) [1], based on Density Functional Theory (DFT) and implemented in the code SCALE-UP. They allow predictive large-scale material-simulations, including both atomic and electronic degrees of freedom, at a very modest computational cost. The method is based on the construction of models written in localized Wannier-functions [2] including electron-phonon and electron-electron corrections.

In this work, we show the results obtained by combining (i) the newly developed code to generate SP models, named MODELMAKER, and (ii) our implementation of real-time (RT) time-dependent (TD) DFT. Fitting the parameters by hybrid-DFT simulations, the models take into account strong electron-electron interactions. Combined with our efficient algorithm to evolve the density matrix in RT, we discuss the influence of these interactions after the system is perturbed by a short electric pulse. Initial results show that electron-hole interactions strongly influence the resulting spectrum, and can be seen using our novel computational technique. This fact, indicates that RT-TD SP-simulations could be a new powerful tool to study excitons at a much smaller computational cost than current methods like the Bethe-Salpeter equation.

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FP-7: Protein-Nanoclusters as Effective Electrocatalyst for the Production of Inkjet Printed Paper Analytical Devices

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Keywords: engineered protein-nanomaterial hybrid, nanoclusters, biosensors, electrochemistry, conductive inks.

Due to the remarkable features that metal nanoclusters exhibit, such as their fluorescence and catalytic properties, they have become increasingly more relevant in sensing applications 1 . The aim of this project is the synthesis of atomic nanoclusters in consensus tetratricopeptide repeat proteins (CTPR) 2 with enhanced catalytic properties and its implementation in biosensors and bioanalytical systems. We have previously proven that nanoclusters can be synthesized using engineered proteins as scaffolds under non-denaturing conditions. The electrochemical characterization of protein-hybrids with different compositions functionalized with electrochemically exfoliated graphene has been studied and the best performing systems were selected. The combination of both materials generates an electrocatalytic synergistic effect that allows the implementation of nanocluster-based systems as a new methodology to perform electrochemical detection. In particular, a proof-of-concept demonstration is focused on the development of a novel hydrogen peroxide biosensor improving the sensitivity of existing detection systems. Furthermore, to achieve a fully automated manufacturing process of the sensor, an inkjet printable ink has been engineered. The efficient electrochemical performance of the formulation was demonstrated by the coupling of glucose oxidase obtaining a glucose selective sensor. Devices printed with these inks showed an analytical performance that is comparable to the commercial screen-printed electrodes available in the market.

Acknowledgments: Agencia Estatal de Investigación, Spain (PID2019-111649RB-I00). DeDNAed (964248).

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FP-8: Determination of Chlorine-Containing Compounds by GC-ICP-MS/MS in Plastic-Based Pyrolysis Oil Samples

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Keywords: GC-ICP-MS/MS, Plastic-based pyrolysis oil, Chlorine, total analysis, speciation analysis.

Plastics recycling has emerged to alternatives such as the production of the plastic-based pyrolysis oil, which has two main uses: the production of new plastics or fuels for engines. However, the presence of halogenated polymers, such as poly (vinyl chloride), as feedstock is a major disadvantage due to the formation of unknown chlorine-containing compounds. These compounds can lead corrosion problems on the engines or damage the catalysts used along industrial production. Due this problem, the presence of chlorine in plastic pyrolysis oils needs to be rapidly detected and, if necessary, characterized.

In this communication, we suggest a methodology for chlorine analysis by GC-ICP-MS/MS based on a previous configuration for sulphur analysis [1]. This approach allows total and speciation quantification analysis for real samples like plastic-based pyrolysis oil samples. The first strategy was carried out with a transfer line and an external calibration, the second one was performed with a chromatography column and with an internal standard. Both quantifications are based on the use of generics Cl-containing standards providing a specie-independent quantification. Using this methodology, it is possible to obtain detection limit of the lower ppb. Different real plastic-based pyrolysis oils samples were analysed applying this methodology, and the concentration values obtained were in good agreement with the alternative approach (combustion followed by Ion Chromatography). The method was validated by a certified reference material.

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FP-9: Kraft Lignin as a Source of Carboxylic Acids by Wet Oxidation

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Keywords: Kraft lignin, carboxylic acids, wet oxidation, black liquor, acid precipitation.

Due to growing environmental concerns, research is focusing on finding renewable and environmentally friendly raw materials to replace non-renewable sources. In this sense, lignin can be a source for the production of biofuels, biochemicals and biomaterials [1]. Therefore, as approximately 50 million tonnes of lignin are obtained each year worldwide in the Kraft black liquor [2], wet oxidation of the precipitated Kraft lignin fraction was studied as a valorisation method for obtaining carboxylic acids.

For this purpose, Kraft black liquor was acidified ($pH<4$) with a sulphuric acid solution and, subsequently, centrifuged. Afterwards, the precipitate (Kraft lignin) was returned to the initial volume and pH. Wet oxidation of this stream was carried out in a 1 L 316 SS semi-batch reactor. The operational conditions used were 700 mL of sample, 1,800 mL O_2/min, 150 rpm, 210 min, 70 bar and from 170 to 210 ºC.

The main physicochemical properties were analysed according to Standard Methods. The concentrations of the organic acids were measured by High-Performance Liquid Chromatography (HPLC). The mobile phase was a solution of sulphuric acid 0.45 mM ($pH = 3.2-3.3$) at a flow rate of 0.3 mL/min and the column (ICSep ICE-ION-300) temperature was maintained constant at 75 °C.

Three volatile fatty acids (formic, acetic and propionic acids) and three non-volatile hydroxy acids (oxalic, malic and lactic acids) were detected.

Wet oxidation caused a continuous reduction of the organic load due to the decomposition of lignin by-products, while organic acids were formed. This resulted in a final reaction medium composed mainly of carboxylic acids, the best temperature being 210 ºC.

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FP-10: A Freeze-Casted Ni/Fe Graphene Oxide Aerogel as a Catalyst for the Electrolysis of Water

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Keywords: graphene oxide aerogels, nickel-iron nanoparticles, freeze-casting, water splitting.

To obtain hydrogen from water splitting, it is necessary to produce low-cost and effective catalysts. A proper material to act as a catalyst precursor is nickel-iron nanoparticles due to their high electrochemical activity. Besides, these nanoparticles can be supported on a graphene oxide aerogel that provides favourable properties like high electrical conductivity, low density, high surface area and good chemical and mechanical stability [1].

These aerogels can be produced by freeze-casting a mixture of graphene oxide and nickel-iron precursor in water suspension. The freeze-casting method consists of pouring an aqueous colloidal suspension into a mould with insulating walls and its subsequent freezing at a controlled rate from the copper bottom of the mould. The freezing rate and the solids content of the suspension influence the size and structure of the aerogel pores, since the ice channels that grow in the sample are lately sublimated by lyophilization [2].

The synthesis of the nickel-iron nanoparticles allowed a water-based processing route for the whole synthesis [3], which helps to obtain a homogeneous dispersion of the precursor in the graphene oxide colloidal suspension. In addition, the exfoliation of large particle-size natural graphite has given rise to large flakes of graphene oxide. The freeze-casting process of the mixed suspensions generated partially reduced graphene aerogels (650 ºC, 4 mg/cm^3) with a pore size of 20-30 µm and nickel-iron particles 15-40 nm in diameter. Using this method, agglomeration of graphene flakes is avoided by the freezing channels present in the aerogel, thus obtaining a large specific surface area and ultradispersing the catalyst along the graphene flakes. All these properties make them a promising material for water splitting.

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FP-11: Halogen Determination in Liquid Samples via Optical Emission Spectroscopy: Towards Online Analysis

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Keywords: LIBS, nebulization, halogen, molecular emission

Determining halogens with emission spectroscopy techniques such as Laser-Induced Breakdown Spectroscopy is a complicated task due to the high excitation threshold of these elements. An approach to this problem is to rely, if possible, on molecular emission resulting from the recombination of the halogen with an alkali-earth metal. For solid samples containing F, a nebulization-assisted LIBS methodology was developed in order to externally provide Ca for the analysis [1] with analogous results of a naturally F and Ca containing sample [2].

This research work provides an application of this concept to liquid sample analysis, which often requires arduous sample preparation procedures and/or complex modifications of the experimental set-up. A nebulization-assisted LIBS system is utilized combining an online liquid sample introduction system with the use of a Ca-containing solid target. Experimental parameters were optimized with a $CaCO_3$ substrate and NaF-containing solutions [3]. Further optimizations were carried out with more convenient Ca-containing targets, for which aqueous samples containing zinc chloride were also prepared, obtaining calibration curves of F, Cl and Zn with LODs of few ppm for F and Zn and ~200 ppm for Cl. A Leave-One-Out Cross Validation procedure was performed to test the prediction robustness of F and Cl calibrations.

In order to test the applicability to complex samples, fluorine content in commercial mouthwashes was adequately determined [3]. Moreover, the total-F determination of a more-challenging sample containing organofluorine was explored, achieving analogous results to those obtained from an inorganic fluoride sample, without further sample preparation.

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FP-12: Phosphane and Quinoline Functionalized Amidinato-Type Heavier Tetrylenes: A New Class of Ligands

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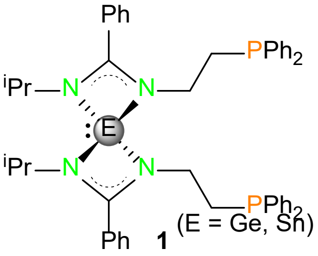
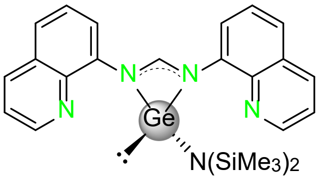
Keywords: heavier tetrylenes, transition-metal complexes, polydentate ligands, amidinates, mechanochemistry.

In the last decade, heavier tetrylenes stabilized by amidinate groups (amidinato-HTs)[1] have emerged as an alternative to classical ligands because they present a strong electron-donor character[2] and their electronic and steric properties can be extensively tuned. These key features are responsible for the interesting catalytic properties shown by many of their metal complexes, particularly by those equipped with polydentate amidinato-HT ligands.[3]

In this field, aiming at expanding the family of polydentate amidinato-HT ligands with possible catalytical applications, our research group has used a functionalization strategy barely explored for these systems, consisting on the attachment of extra coordinable groups to the amidinate N atoms. This particular contribution describes the synthesis of novel polydentate amidinato-HTs that feature two phosphanes or two quinolines and one HT as potential coordinating groups (ligands **1** and **2**), and a preliminary inspection of their coordination chemistry. Additionally, we have proven that ligands **1** and some of their metallic complexes can be made with no solvent (or a minimum amount of it) using mechanochemical methods,[4] which have no precedents for the synthesis of heavier tetrylene derivatives.



1 (E = Ge, Sn)



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Acknowledgments: Projects PID2019-104652GB-I00 and RED2018-102387-T (MCI, Spain)

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FP-13: Stacked Archimedean Spirals Reactor with Porous Carbon Walls, Made From 3D Printed Sacrificial PLA Moulds

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Keywords: additive manufacturing, 3d printing, porous carbon, whey.

Introduction: Nowadays it is relatively easy to obtain complex pieces from a wide variety of materials, mainly polymers, but also other families like ceramics or metals. However, in the case of porous carbons, this is not so simple. High temperature thermal processes are often incompatible with shape conservation for most carbon precursors. The combination of 3D printed sacrificial moulds of polylactic acid (PLA) with whey powders as a carbon precursor, allows to obtain porous carbon pieces with complex designs. In this work, a porous carbon-walled reactor designed as two stacked Archimedean spirals is shown as an example.

Materials and methods: the carbon pieces were obtained by: i) printing the sacrificial mould ii) embed the mould in a bed of whey powders, iii) curing the piece, to assure its consistency, at 150°C and iv) carbonising the piece.

Results and discussion: PLA is a common material used as a filament in 3D printing devices. The use of sacrificial PLA moulds is based in the thermal behaviour of this polymer at high temperatures. As shown in Figure 1, after carbonization, the PLA totally disappear (<2% of residue). On the other hand, whey powders act as a thermosetting resin that maintains geometry after carbonization. These two facts together allow the obtention of complex pieces which are impossible to produce using any other technique. In this case, the selected design has been a pipe in the form of stacked Archimedean spirals, in order to maximize the contact surface for a hypothetical catalytic reactor made of porous carbon.

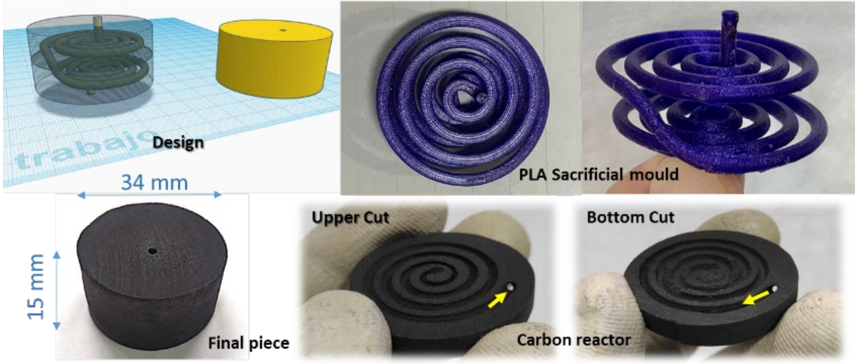

Figure 1 Sacrificial PLA moulding process

Acknowledgments: (The authors gratefully acknowledge the financial support received from the Ministerio de Ciencia e Innovación (MCIN/AEI/10.13039/501100011033) (Project PID2020-115334GB-I00) and Principado de Asturias (FICYT) - European Union (FEDER) (Project PCTI-Asturias IDI/2021/000015).

FP-14: One-Pot Diastereoselective Synthesis of Indolizidine and Pyrrolo-[1,2- a]Azepine Heterocycles

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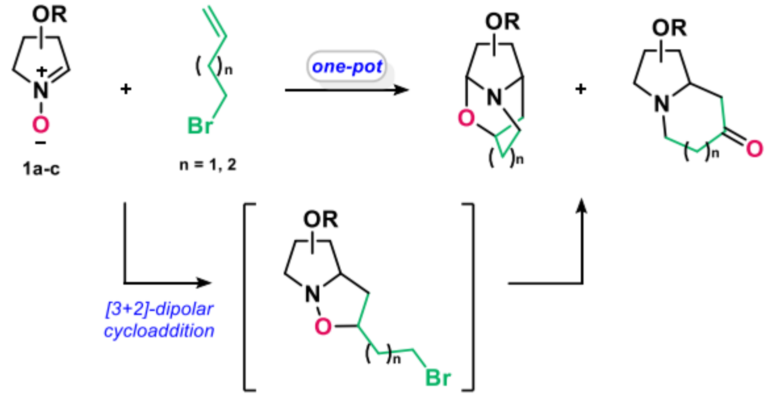
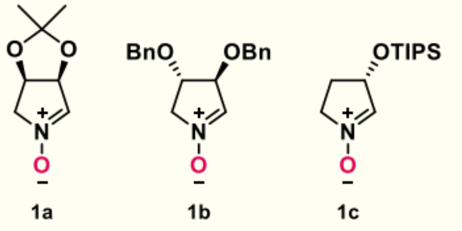
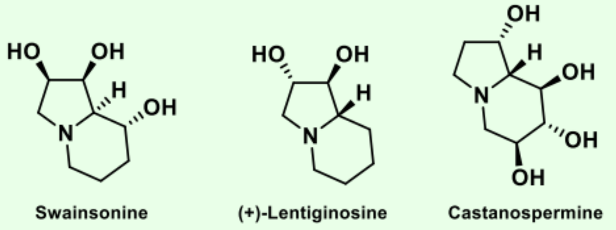
Keywords: Indolizidine, pyrrolo[1,2-a]azepine, diastereoselective cycloaddition

Indolizidines and pyrrolo[1,2-a]azepines are prominent scaffolds in a variety of biologically active molecules. 1 Cycloaddition of nitrones with olefines constitutes a traditional approach to obtain these azabicyclic core through isoxazolidine intermediates.2 In this context, we recently reported the diastereoselective [3+2]-dipolar cycloaddition of nitrones 1a-c with brominated alkenes which leads to these heterocycles in one-step.





Selected nitrones



Natural indolizidine alkaloids

Acknowledgments: We thank the government of Castilla y León (SA076P20) and Spanish Ministry of Science and Innovation (PID2020-118303GB-I00) for financial support, N. G. L. thanks Universidad de Salamanca and Banco Santander for predoctoral grant.

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FP-15: ICP-MS Based Characterization of Biogenic SeNPs and Evaluation of their Potential Antibacterial Activity

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Keywords: Biogenic nanoparticles, ICP-MS, single particle-ICP-MS, antibacterial activity, MIC.

Selenium (Se) is a chemical element whose compounds have been reported as antimicrobial, antioxidant and anticarcinogenic agents. Its nanoparticulated form (SeNPs) arose great interest in the field of biomedicine, as its particular physicochemical characteristics confer lower toxicity, as well as greater bioavailability with respect to other selenium species [1]. Biogenic SeNPs, which are synthesized by biological systems such as plants, bacteria, or fungi, present a greater biocompatibility and stability in contrast to the ones produced by means of chemical processes. Moreover, their biological origin can confer them special behaviour and physiological properties, which grant this type of NPs special relevance from a biomedical point of view [2].

In this work, different species of edible fungi, cultivated in a selenite enriched medium, have been studied as potential biogenic nanoparticulated selenium producers. Following an optimization of the extraction method to isolate the nanoparticles, single particle analysis by ICP-MS (SP-ICP-MS), formerly reported for the characterization of individual selenium nanostructures in yeast [3], was applied successfully in this work to address the presence, characteristics, and number concentration of SeNPs in the mentioned fungi samples. Additionally, after the nanoparticle extraction and characterization, their antibacterial activity was evaluated by means of several bioassays that were carried out employing different bacterial species cultures. These allowed to obtain the MIC value (minimum inhibitory concentration) of the studied SeNPs.

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FP-16: Characterization of a Chemical Bias Shaping Microbial Functional Evolution

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Keywords: Phylogeny, chemical landscape, functional evolution, structure convergency.

The study of biological functions in microbiomes is prohibitively difficult, both in terms of information quantity and ambiguity. Phylogenetic reconstruction of biostructures can help discriminate groups of sequences with similar functional behavior. In this work, we measured the effect of the physicochemical environment on the dissimilarity groups of orthologs of potF, a subunit of an ABC transporter that binds putrescine and other polyamines. For this we construct a vector of chemical properties to which the organisms present in the reference phylogenetic tree are subjected and check with a null model how enriched the nodes are for which environmental properties, considering the tree topology. The result shows that there would be sequences that, although their phylogenetic position is distant, appear with similar sequences, indicating environmental convergence. These results have an important connotation in the framework of molecular evolution, as they indicate that there is evolutionarily relevant information contained in the chemical landscape that affects the fitness of biologically functional quasispecies.

Acknowledgments: Juan F. Poyatos Adeva.

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FP-17: Magnetic MoS_2 Based Nanocomposites for the Photodegradation of Pollutants

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Keywords: MoS_2, Magnetic, Photocatalyst, Acetamiprid

The agro-food industry produces large amounts of water namely in fruit and vegetables' washing and cleaning processes.[1] Due to the high concentration of pesticides, the wastewater can no longer be reused and is discharged into wastewater treatment units, where the treatments employed might be non-effective in removing such contaminants.[1] Acetamiprid is an insecticide commonly used in this context, namely to control Hemiptera spp. proliferation in fruit, vegetables and ornamental plants and flowers. Several methods have been developed to remediate the presence of acetamiprid and other pesticides in wastewater discharged into treatment units.[1] Photocatalysis is a low-cost and clean method that enables the removal of contaminants.[2] Among the transition metal dichalcogenides, MoS_2 nanomaterials have proved to be effective in removing water contaminants by photocatalysis processes.[3] Moreover, the combination of these materials with magnetic particles impart to the ensuing nanocomposites the ability for easy, fast and cost-less recovery of the catalysts by magnetic separation.[3]

In this work, composite nanostructures of MoS_2-Fe_3O_4 were produced by a new hydrothermal method. The nanostructures were characterized by transmission electron microscopy and powder X-ray diffraction, N_2 sorption isotherms and FTIR spectroscopy. For preliminary studies, a Rhodamine B solution degradation was verified via UV-Vis spectroscopy at λ=554 nm. In further studies the photodegradation of acetamiprid spiked in water samples was investigated. The concentration of acetamiprid in the aqueous samples was monitored using HPLC. The performance of the MoS_2-Fe_3O_4 nanomaterials as multifunctional photocatalyst is discussed based on their potential for subsequent regeneration.

Acknowledgments: L. Amaral thanks the Fundação para a Ciência e a Tecnologia (FCT) for the PhD Grant UI/BD/151138/2021. This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC).

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FP-18: One-Step Synthesis of BODIPY Dyes and Analogues Under Microwave Irradiation

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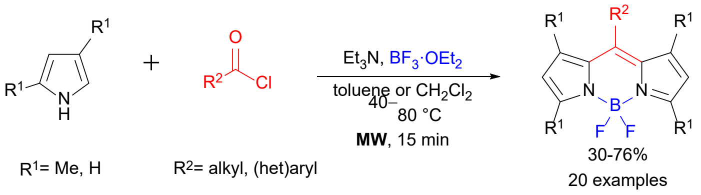
Keywords: BODIPYs, one-step synthesis, microwave irradiation

Boron dipyrromethenes compounds (BODIPYs) are a family of fluorescent organic dyes that have received great interest in recent years due to their attractive chemical and photophysical properties including their stability and high lipophilicity. These interesting properties make them suitable for a wide range of applications in numerous fields of chemistry, biology, medicine and materials.[1] In spite of their wide application, the synthesis of BODIPY derivatives is neither efficient nor practical yielding the target molecules in low to moderate yields requiring long reaction times. In this communication we report the one-step synthesis of BODIPY dyes from available pyrroles and acyl chlorides under microwave irradiation.[2]

The one-pot reaction is performed by mixing a variety of pyrroles and acyl chlorides in the presence of $BF_3{\cdot}OEt_2$ and Et_3N in CH_2Cl_2 irradiating the mixture with microwaves for 15 minutes at 40 °C giving rise the BODIPYs in a good yields. This method can be also extended to obtain other analogues such as BOPHYs, BOAHYs and BOPAHYs, prepared from 2-carbonyl pyrroles and hydrazines or hydrazides. The intrinsic advantages of this practical and environmentally friendly one-pot process are short reaction times, moderate temperatures, minimum amount of solvent used, scalability, versatility, and good yields of the products.



Acknowledgments: We are grateful to the Ministerio de Ciencia, Innovación y Universidades (PGC2018-097792-B-I00 and PID2021-122335NB-I00) and Xunta de Galicia (GRC2018/039 and GRC2022/039) and EDRF funds for financial support. ADL thanks the Xunta de Galicia for predoctoral fellowship (ED431B2020/52).

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FP-19: Determination of GFAP Biomarker in Human Serum Using Metal Nanoclusters as Label by Elemental Mass Spectrometry and Cyclic Voltammetry

Alejandro Rodríguez-Penedo[1]*, Beatriz Fernández[1], Estefanía Costa-Rama[1], C. García-Cabo[2], L. Benavente[2], S. Calleja[2], M. Teresa Fernández-Abedul[1], Rosario Pereiro[1]

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Keywords: GFAP, Stroke, Palladium nanocluster, Electrochemistry, Mass Spectrometry

Stroke is one of the most frequent causes of death in Spain; it currently affects more than 100,000 people, 15% of whom die and a large number of survivors suffer permanent sequelae. There are two types of strokes, ischemic and haemorrhagic, and it is necessary to identify the type of stroke that is occurring before starting an effective treatment. The time from stroke to initiation of treatment is crucial to reduce both mortality and permanent sequelae, so there is a strong interest in developing accurate methodologies for rapid and decentralized differentiation.

GFAP has been recently found to be a biomarker for early stroke type differentiation [1]. Due to its low concentration in biological fluids, it’s necessary to resort to sensitive analytical techniques for its accurate determination. In recent years, considerable progress has been made in the use of antibodies labelled with elemental labels for the development of sensitive analytical immunoassays [2]. In this vein, metal nanoclusters (MNCs) have been presented as excellent tags for determination of target analytes in biological fluids. MNCs are spherical clusters of a unique metal atom (with diameters below 3 nm) and their properties include a good stability and ease of bioconjugation (the surface of the nanostructure can be tailored with selected groups for different chemistries).

In this work, the synthesis of PdNCs was developed to obtain highly stable, monodisperse and water soluble nanostructures with diameters below 2.5 nm composed of more than five hundred atoms. PdNCs exhibit catalytic activity on hydrogen evolution reaction (HER) and, thus, it has been employed as specific label for the biomodal determination of GFAP protein in human serum samples both by cyclic voltammetry and elemental mass spectrometry (ICP-MS). Analytical immunoassays were carried out using serum samples from control donors as well as patients diagnosed with stroke (both haemorrhagic and ischemic).

Acknowledgments: This work was financially supported through project AYUD/2021/51289 (PCTI Program of the Government of the Principality of Asturias and FEDER Program of the European Union) and PID2019-107838RB-I00/Agencia Estatal de Investigación (AEI)/10.13039/501100011033) in Spain.

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FP-20: Synthesis of Benzannulated Spiroketals by Indium-Catalyzed Intramolecular Double Dihydroalkoxylation of Alkyne Diols

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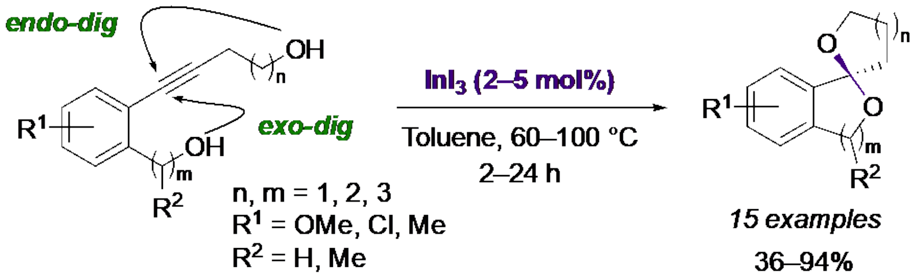
Keywords: Indium(III), main group metal catalysis, cycloisomerization, spiroketal

During the last years, indium(III) has been shown as an useful as π-Lewis acid for the catalytic electrophilic activation of unsaturated systems.[1] In this research area, our group has developed an increasing number of cycloisomerization reactions under indium catalysis.[2] Herein, we present the first In(III)-catalyzed intramolecular double dihydroalkoxylation of *o*-(hydroxyalkynyl)benzyl alcohols for the synthesis of benzannulated spiroketals.[3] The reaction proceeds using indium triiodide (2-5 mol%) as catalyst, with high regioselectivity with a variety of *o*-(hydroxyalkynyl)benzyl or homobenzyl alcohols providing access to a variety of spiroketals in good yields.

A plausible mechanism is initiated with the indium(III) electrophilic activation of the alkyne followed by intramolecular *anti* addition by one of the hydroxyl groups, a second hydroalkoxylation and final protodemetallation gives the spiroketal. Experimental results and NMR studies to determine the reaction mechanism will be presented and discussed.



Acknowledgments: We thank Ministerio de Ciencia, Innovación y Universidades (PGC2018-097792-B-I00 and PID2021-122335NB-I00), Xunta de Galicia GRC2018/039 and GRC2022/039) and EDRF funds for financial support. RPG thanks Xunta de Galicia for a predoctoral fellowship.

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FP-21: A Three-Pollutant Simultaneous Photodegradation. $BiOX_xY_{1-x}$ (X=Br or Cl; Y=I) as a Photocatalytic Solution for Water Treatment

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Keywords: Bismuth oxyhalides, photocatalyst, emerging contaminants, visible light, simultaneous degradation.

The growth of world population and industrial activity has led to an increase in the pollution of emerging contaminants (EC) in rivers, lakes, and drinking waters, becoming a global matter of concern. Removing these EC is a great challenge, being photocatalysis one of the most efficient strategies to solve this issue since solar light is an abundant and cheap power source. However, the examples in the literature are mostly focused on the degradation of a single contaminant [1], while real wastewater contains a wide range of pollutants. Therefore, the study of the simultaneous degradation of several contaminants is paramount to testing the real efficiency of the semiconductor. Bismuth-based materials are promising candidates to be used as photocatalysts for this purpose since they show outstanding properties such as stability, easy modification, non-toxicity, and visible-light-driven photocatalytic activity.[2]

In this work, we present a one-pot synthesis of several bismuth oxyhalides, $BiOX_xY_{1-x}$ (X=Br or Cl; Y=I), at room temperature. A full characterization of the materials has been performed, focusing on their structural and optical properties. Methylparaben (from personal-care products), rhodamine B (industrial dye), and ciprofloxacin (antibiotic) were chosen as model compounds for the test of photocatalytic activity. The materials were tested for the simultaneous degradation of the three pollutants in the water solution achieving the elimination of the three substances simultaneously.

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FP-22: Detection of MMP-9 Biomarker Using Nanochannels

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Keywords: MMP-9, biomarker, nanochannels, nanopores, biosensing

Cancer can be considered a leading cause of death and disability. Among different types of cancers, breast cancer is one of the most common with about 2.26 million cases in 2020. Early diagnosis with a rapid treatment can be highly effective, reaching 90% probabilities of survival. On this purpose, biomarkers monitoring is a useful approach for cancer diagnosis. Among different biomarkers matrix metalloproteinase-9 stands out, as a protease that plays an important role in the tumour metastasis and invasion of cancerous cells being overexpressed in breast cancer [1].

Biosensing systems based on nanoparticles and nanochannels emerge here as outstanding tools for fulfilling such social demand. In particular, the use of nanopores/nanochannels has shown an enormous growth in the last decade, becoming one of the most promising fields of research in the biosensing area [2]. Nanoporous alumina membranes stand out from these materials, due to their easy functionalization, capacity for mass production and biocompatibility [3,4].

In this context, we propose a novel methodology for the detection of matrix metalloproteinases (MMPs) using nanoporous alumina membranes. The methodology is based on the blocking of the nanochannels by a peptidic substrate, and the specific unblocking by the protease activity of the MMP-9. The nanochannels blocking/unblocking is voltammetrically monitored through the diffusion of a red-ox indicator, using indium tin oxide/poly(ethylene terephthalate) (ITO/PET) electrodes.

Acknowledgments: We acknowledge MICINN (Spain) for the project MCI-21-PID2020-115204RB-I00, the FPI grant (PRE2021-097567; D. Valero-Calvo), the FPI grant (PRE2018-084853; C. Toyos-Rodríguez) and the 'Ramón y Cajal' fellowship (RyC-2016-20299; A. de la Escosura-Muñiz). Asturias Regional Government is also acknowledged for the project SV-PA-21-AYUD/2021/51323.

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FP-23: Design of a Hybrid One-Pot Tandem Combination of the Cu(II)-Catalyzed Oxidation of Alcohols with an Enantioselective Organocatalyzed Aldol Reaction

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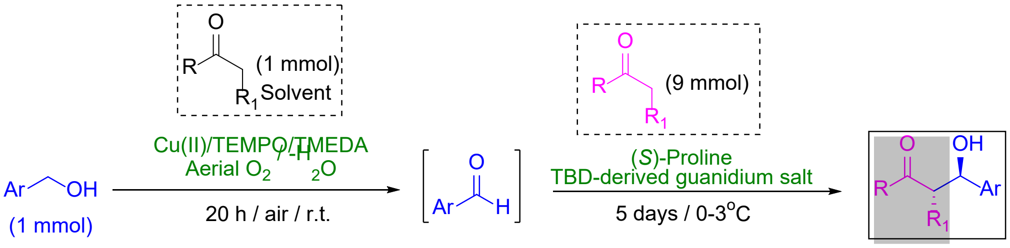
Keywords: Hybrid One-Pot Reactions, Cu-oxidation, Organocatalysis, Aldol Reaction.

Since the last decade and in the framework of organic synthesis, the design of one-pot tandem protocols is occupying a strategic place as new greener methodologies replacing standard and tedious stepwise synthetic processes[1]. In these one-pot tandem approaches, one of the most difficult challenges to solve is the design of hybrid protocols in which different synthetic organic tools are assembled in the same reaction media[2]. In this sense, our group is developing an unprecedented methodology that combines the oxidation of primary alcohols into aldehydes by using a $CuCl_2$/TEMPO/TMEDA catalytic system [3] (note that the unwanted formation of acids is not observe and aerial O_2 is used as the oxidant), with the organocatalyzed [(*S*)-proline and a TBD-derived guanidium salt] and enantioselective aldol reaction of the *in-situ* generated aldehydes with different ketones[4]. Thus, our aim is to provide a simple but efficient, selective and straightforward methodology for the synthesis of chiral aldols (starting from raw materials) in which no isolation or purification of intermediates is needed.



Acknowledgments: PID2020-113473GB-I00; PA-22-PF-BP21-088.

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FP-24: Very Efficient Organo-Zinc Scorpionates for the CO_2 Fixation into a Variety of Cyclic Carbonates

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Keywords: Organo-Zinc complexes, scorpionates, CO_2 fixation, cyclic carbonates.

Fixation of CO_2 into cyclic carbonates is urgently required under green and eco-friendly conditions. Herein, we described a series of easy-prepared and robust sterically demanding scorpionate zinc-based mononuclear complexes [ZnMe(κ^3-phbp^{t}amd)] **1** and [ZnCl(κ^3-phbp^{t}amd)] **2**, in combination with the use of co-catalysts comprising larger ionic radius-based halides such as tetra-*n*-butylammonium, resulted in very active and selective catalysts for CO_2 fixation into five-membered cyclic carbonates. [1] These studies have led to the development of a sustainable, inexpensive, and low-toxic system formed by **1** and Bu_4NBr for the cycloaddition of CO_2 into epoxides under very mild and solvent-free conditions, reaching very good to excellent conversions (TOF = 260 h^{-1}). Moreover, this bicomponent system shows a wide range of substrate scope and functional group tolerance, including mono- and di-substituted epoxides, as well as bio-renewable diepoxides (Figure 1). Very interestingly, this is the first zinc-based system reported to date for the successfully transformation of the very challenging tri-substituted terpene-derived *cis*/*trans*-limonene oxide, whose reaction proceeds with high stereoselectivity to the formation of the bicyclic *trans*-limonene carbonate. Additionally, this bicomponent system can be up to six-times efficiently fed without significant loss of activity. Kinetic investigations confirmed that the reaction follows an apparent first-order dependence on the catalyst and co-catalyst concentrations, which supports an intramolecular monometallic mechanism.

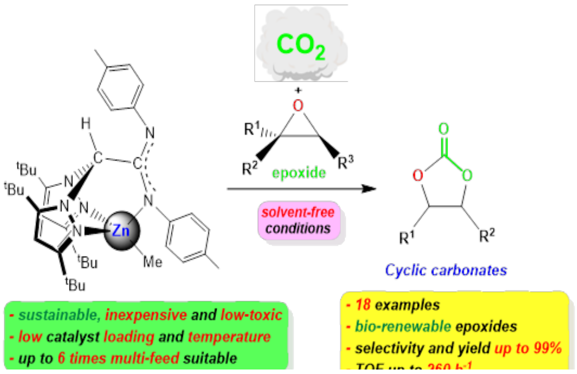

Figure 1. Representative scheme of CO2 fixation catalysis in epoxides.

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FP-25: Halogen-Bonding Assisted Generation of Vinyl Radicals: Stereoselective Cross Coupling Between Thiols and Vinyl Halides

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Keywords: photochemistry, halogen bonding, radical disconnection, stereoselective, crosscoupling

The photochemical halogen-bonding assisted generation of radicals has risen in the last years as a powerful synthetic tool for the creation of radical intermediates under mild reaction conditions.[1] However, this reactivity has up to date been restricted to the generation of aryl and alkyl radicals. The formation of vinyl radicals from the corresponding alkenyl halides stands as a challenging approach under operationally simple and mild conditions, given the low stability for the first ones and high reduction potentials of the second ones.[2] We envisioned that the halogen bonding assisted generation of vinyl radicals would be a feasible process in the photochemical cross coupling reaction between vinyl halides and thiols under basic conditions.

✓ Catalyst-free ✓ FG tolerance ✓ Operationally simple ✓ Visible light

The reaction indeed shows a very broad functional group tolerance, is stereoselective, simple and scalable. In-depth mechanistic studies point at the formation of vinyl radical intermediates and DFT calculations support the formation of a halogen-bonding complex as the initiator of the photochemical reaction under visible light irradiation (440 nm). This new methodology could also be applied to the synthesis and modification of biologically active molecules.[3]

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FP-26: Supramolecular Self-Assembly of Metal-Metal Bonded Species

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Keywords: Supramolecular chemistry, diruthenium, paddlewheel, hydrogen bonding, magnetic properties.

Diruthenium complexes with appropriate structural features have been designed in order to study different supramolecular self-assembly processes. The synthesis of these species can be carried out following different experimental procedures, including solvent refluxed, solvothermal microwave-assisted and ultrasound assisted syntheses, achieving a huge versatility of structures. Using $[Ru_2Cl(\mu\text{-}O_2CCH_3)_4]$ as the starting product, it is possible to substitute acetate ligands in a controlled manner to form more stable compounds of the type $[Ru_2Cl(\mu\text{-}N,N')_x(\mu\text{-}O_2CCH_3)_{4-x}]$ (x = 1 – 4; N,N' = formamidinato ligands). These complexes will be the basis for preparing compounds of the type $[Ru_2Cl(\mu\text{-}N,N')_x(\mu\text{-}X,X')_{4-x}]$, in which *X,X'* will be strategically chosen ligands to facilitate self-assembly.

For this purpose, the $[Ru_2Cl(\mu\text{-A})(\mu\text{-DPhF})_3]$ and $[Ru_2Cl(\mu\text{-DPhF})_3(\mu\text{-UAc})]$ (DPhF = *N*,*N*'-diphenylformamidinate, A = adenine, UAc = uracil-4-acetate) complexes (Figure 1a) have been synthesized, in first place. The existence of association processes in these species in solution has been determined by electronic spectroscopy measurements at variable concentration. This association occurs through Watson-Crick hydrogen bonding interactions (Figure 1b). Secondly, *cis*-$[Ru_2Cl(\mu\text{-DAniF})_2(\mu\text{-}O_2CCH_3)_2]$ and *trans*-$[Ru_2Cl(\mu\text{-DXyl}^{2.6F})_2(\mu\text{-}O_2CCH_3)_2]$ complexes (DAniF = *N*,*N*'-bis(*p*-methoxyphenyl)formamidinate, DXyl$^{2.6}$F = *N*,*N*'-bis(2,6-dimethylphenyl)formamidinate) (Figure 1c) have been prepared. Despite the paramagnetic nature of these compounds, the self-association process of these species, giving rise to oligomers through bridging chloride ligands, has been studied by proton nuclear magnetic resonance at variable concentration.

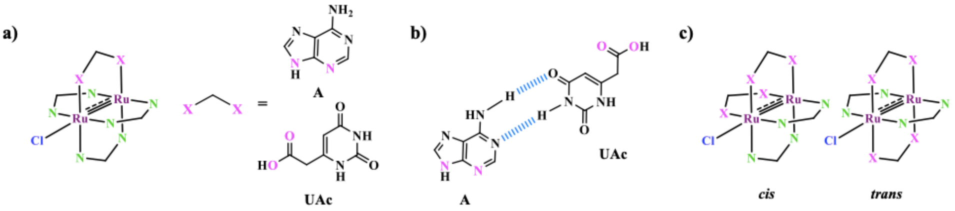

Figure 1. Scheme of a) triformamidinato and proposed X-X ligands. b) Complementary Watson-Crick hydrogen bonding between adenine and uracil-4-acetate. c) Diformamidinato diruthenium species.

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FP-27: Catalytic Cyclopropanation Reactions with α-Silyl-, Germanyl- and Stannyl Carbenes Generated from Cyclopropenes

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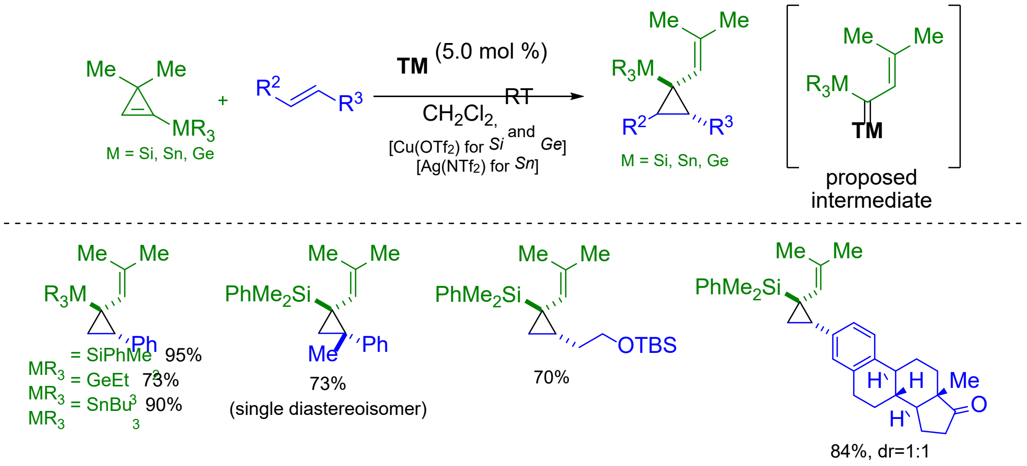
Metal carbenes are valuable synthetic intermediates, and their uses in catalytic cyclopropanation of alkenes constitutes one of the most characteristic reaction of metal carbenes.[1][2] Indeed, our group recently reported intermolecular metal-catalysed alkene cyclopropanation using 3,3-disubstituted cyclopropenes as a precursor of metal carbenes.[3]

We reported the use of silylcyclopropenes as precursors of α-silyl vinyl carbenes and their subsequent trapping with alkenes. Thus, a variety of cyclopropylsilanes are obtained in good yields with complete regio- and diastereoselectivity. Cyclopropylstannanes and -germanes can also be prepared from the corresponding cyclopropenes.[4]



Keywords: Cyclopropenes, metal carbenes, cyclopropanation

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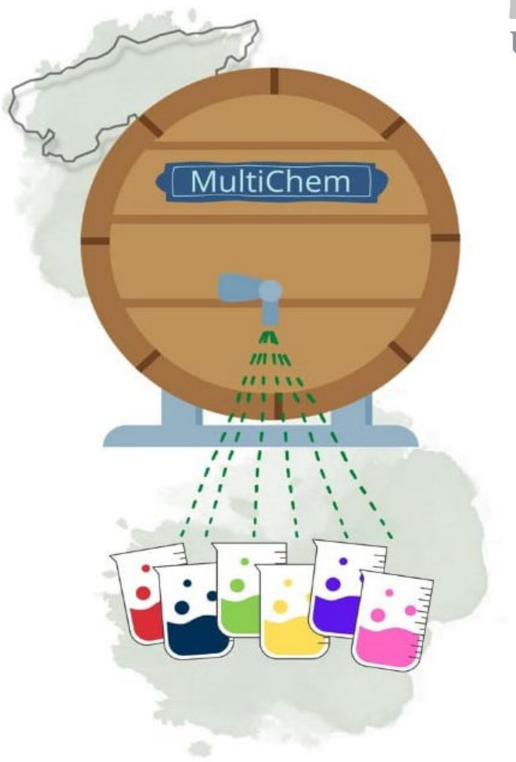

POSTERS

PO-1: Characterisation of Binding Properties of Thermoresponsive Peptide Imprinted Nanoparticles

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Keywords: Molecularly imprinted polymers, artificial antibodies, solid phase synthesis, epitope imprinting.

Molecularly imprinted polymers (MIPs) are many times referred to as antibody mimics, since they are synthetic structures that selectively recognise a certain ligand with affinities comparable to their natural counterparts (1). This work deals with MIPs synthesised in nanoparticle format, as artificial anti-CB1 antibodies. This has been achieved combining the solid phase and the epitope imprinting approaches, using a linear peptide of 15 amino acids as template, which matches the final C-terminal fraction of the cannabinoid CB1 receptor (458-KVTMSVSTDTSAEAL-472). This sequence is responsible for the desensitization and internalization of the CB1 receptor as it is involved in the coupling of $G_{i/o}$ proteins intracellularly (2).Some monomers used in the synthesis process, such as N-isopropylacrylamide, are known to provide stimuli responsive polymers. In this regard, produced nanoparticles have shown to undergo a volume phase transition from coil to globule conformation upon temperature change (3), that is, they present thermoresponsive behaviour. As detailed in the literature (4), increasing the crosslinker amount in the polymerisation mixture produces nanoparticles with higher rigidity, which makes them lose their temperature responsiveness. Based on this premise, the effect of the crosslinker amount on the resulting imprinted nanoparticles (MIN) was assessed here, preparing a series of MIN with increasing levels of crosslinker. Turbidity assays demonstrated that higher crosslinker levels made the lower critical solution temperature (LCST) decrease, being the transition from coil to globule faster. Additionally, binding experiments were performed using a 50 µg/mL suspension of MIN and increasing levels of the peptide ligand in order to determine how the thermoresponsive behaviour influenced MIN affinity.

Acknowledgments: project CTQ2017-85686-R and Research Groups of the Basque University System, Project No IT 1492–22.

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PO-2: An in Vitro Bioaccessibility Assessment of Trace Elements in Recreational City Areas

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Keywords: urban, soil, metal, bioaccessibility, in vitro.

Urban soils may contain different heavy metals of varying toxicity that appear as trace elements with an average concentration of less than 100 $mg \cdot kg^{-1}$. Cu, Hg, Pb and Zn are the most typical urban trace elements [1,2]. These elements can enter the human body by direct inhalation, ingestion or dermic absorption [3]. According to USEPA, United States Environmental Protection Agency, 200 mg/day is the average daily ingested dose of soil for children aged from 1 to 6, and 100 mg/day for people between 7 and 70 years [4]. Recently, in vitro methodologies have been proposed for the quantification of the metal fraction mobilized from soils during the digestion process, that is, the bioaccessible trace metal fraction. Simplified Bioavailability Extraction Test (SBET) simulates human digestion using a synthetic gastric solution. The stomach fluid is prepared by dissolving 60.06 g of glycine in 2 L of deionized water and adjusting to pH 1.5 with HCl [5]. After mixing for 2 hours, the digested trace metal fraction is analysed. A total of twenty-seven urban soils were collected in July 2022 from parks and leisure areas from San Sebastian to evaluate the adverse health effects of the exposure of population to trace elements. In order to study the effects that typical city activities could have in the quality of soils, parks chosen for the study included areas close to industrial activities, deep traffic, coast, etc. Soil samples were dried, sieved below 2 mm and physical-chemical parameters as pH, electrical conductivity and organic content were examined in order to assess their influence on bioaccessibility of metals. Then, SBET digestion was simulated and the solution was filtrated and analysed by ICP-MS. Results showed significant spatial differences in terms of bioaccessibility, obtaining significantly higher values for zinc, copper and lead in areas more exposed to city activities.

Acknowledgments: Ainhoa Lekuona is grateful to the University of the Basque Country because of her pre-doctoral grant.

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PO-3: Novel Synthetic Methodologies Lead to Cocaine Analogues and New Bioactive Heterobicycle Compounds

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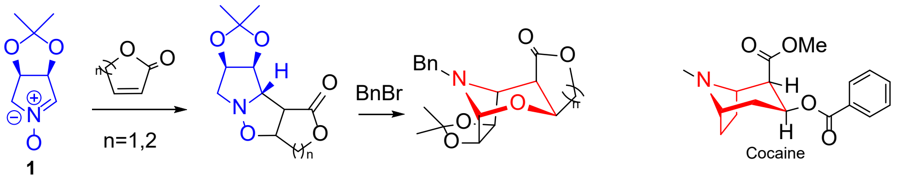
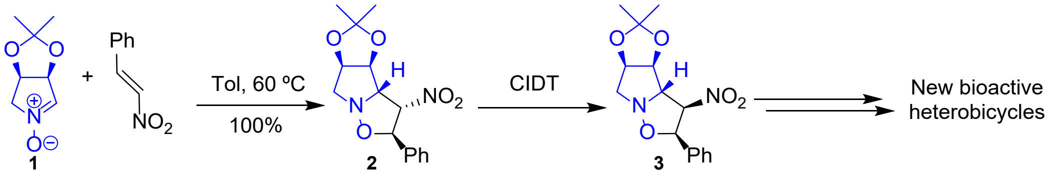
Keywords: Tropane alkaloids, rearrangements, nitro compounds, heterobicycles.

8-azabicycle[3.2.1]octane systems are particularly relevant because of their strutural similarity with tropane alkaloids as cocaine. [1] A novel rearrangement reaction, recently discovered in our group, lead to the synthesis of new tropane analogues (Scheme 1) [2] opening a broad unexplored chemical space.



Scheme 1: Synthesis of cocaine analogues.

In the pursuit of new isoxazolidine cores as precursors, the problematic synthesis of 4-nitroisoxazolidines was solved by a Crystallization-Induced Diastereomer Transformation (CIDT) process (Scheme 2). The stablished methodology enables the synthesis of new bioactive heterobicycle compounds.



Scheme 2: CIDT effect in new isoxazolidine core synthons. [3]

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PO-4: First Steps in the Development of Stimuli-Responsive Pyridinium-Based Supramolecular Amphiphiles

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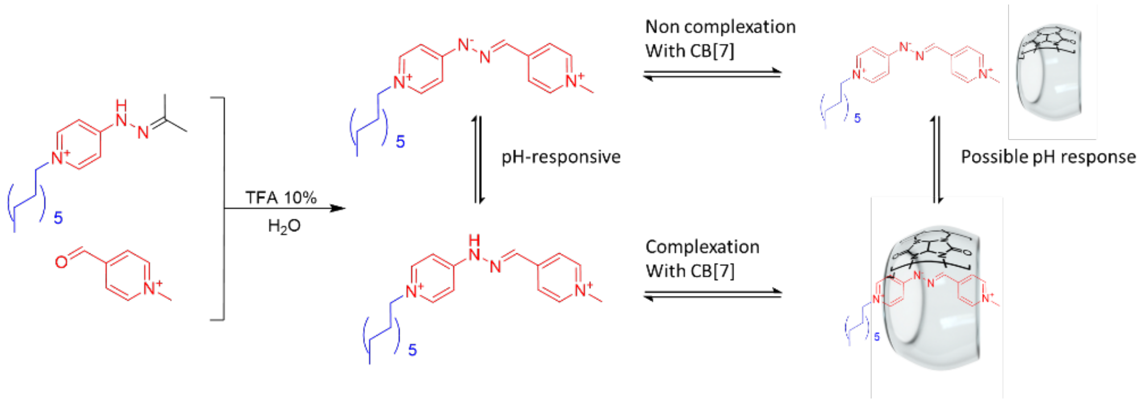
Keywords: Supramolecular chemistry, amphiphiles, vermellogens, cucurbit[n]urils.

The use of amphiphilic molecules as building blocks for liposomal systems has established itself as one of the most promising options for the delivery of drugs and other molecules of biological interest. This kind of system helps to dissolve, protect and distribute the cargo in the organism. However, low release control and unspecificity make it necessary to develop new stimuli-responsive amphiphilic compounds capable of modifying their aggregation and therefore regulating the release of the molecule of interest.1 Based on the recent results reported by our research group in the development of a new family of viologen-based compounds (vermellogens) that behave as pH-responsive supramolecular switches with CB[7] and CB[8],2 we present herein the synthesis and characterization of a new vermellogen-based amphiphile. In addition, we show preliminary results through 1D/2D NMR and DOSY of the formation of inclusion complexes of our amphiphile with CB[7] and their aggregation at pH 7 and 11. These are the first steps toward obtaining a pH-responsive and complexation-responsive liposomal system.



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PO-5: Photochemical Metal-Free C(sp3)–C(sp3) and C(sp3)–B Bond Forming Reactions Employing N-Tosylhydrazones and Boronic Acids

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Keywords: Photochemistry, Metal-free, Boronic acid, *N*-tosylhydrazone, Cross-coupling.

Our research group has pioneered since a seminal work developed in 2009 different metal-free cross-coupling reactions involving *N*-tosylhydrazones and boronic acids [1]. These transformations are operationally very simple to run: only both coupling reagents, a base and the solvent are needed under heating conditions to furnish the desired products. The highly reactive boronic acid intermediates that are transiently formed in these processes have been exploited for various C–H/C–C bond forming reactions [2] and also different cyclizations in which two different C–X bonds are generated on the same carbon atom in one step [3]. We have now developed a new photochemical reaction in which, due to unprecedently mild room temperature reaction conditions for this kind of transformations, highly reactive benzyl boronic acid intermediates (green box) could be trapped for the first time under latter exposure to pinacol to form the corresponding boronic esters. This reaction represents a novel and elegant strategy for the modular generation of high-added-value boron-containing molecules, which are widely used nowadays in medicinal chemistry. Iterative procedures for the modular construction of more complex C(sp^3) enriched boron compounds are currently being explored.

Acknowledgments: Financial support of this work by Ministerio de Ciencia e Innovación of Spain is gratefully acknowledged (Agencia Estatal de Investigación: PID-2019107580gb-I00/AEI/10.13039/501100011033).

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PO-6: Synthesis and N–O Bond Activation of Binuclear Complexes with Bridging Nitrosyls in Unusual Coordination Modes

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Keywords: Binuclear complexes, nitrosyl ligands, coordination modes, N-O bond activation

Nitric oxide is a versatile ligand able to bind metal atoms in both high and low oxidation states giving rise to a wide variety of complexes where the nitrosyl ligand displays different coordination modes. Although NO is essential from a biological point of view (it acts as a neurotransmitter, regulates blood pressure, etc) it is also one of the main air pollutants that contributes to the greenhouse effect, acid rain, etc, thus requiring catalytic abatement. The latter involves the cleavage of the N–O bond that can be facilitated by the presence of electronic or coordinative unsaturation at a metal center. [1] This is why we have been studying for some time the chemistry of binuclear nitrosyl complexes bearing different sorts of unsaturation, as they are molecular sites potentially able to activate (weaken) and eventually cleavage the nitrosyl N–O bond at a dimetal site. [2] We hereby report some complexes with bridging nitrosyl ligands that can undergo different bond activation and cleavage reactions.

The new nitrosyl bridged complex, $[M_2Cp_2(\mu\text{-}P^tBu_2)(\mu{:}\kappa{:}\eta\text{-}NO)(CO)(NO)][BAr'_4]$, is made from the corresponding hydride $[M_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(CO)_4]$ (**1**), via $[M_2Cp_2(\mu\text{-}P^tBu_2)(CO)_2(NO)_2][BX_4]$ (**2**) and $[M_2Cp(\mu{:}\kappa{:}\eta^5\text{-}C_5H_4)(\mu\text{-}P^tBu_2)(CO)(NO)_2]$ (**3**) (M = Mo, W; BX_4 = BF_4, BAr'_4). In this complex the N–O ligand displays a $\kappa{:}\eta$ coordination mode, whose reactivity has not been studied before, with an elongated N–O distance, resulting in a bond weaker than terminal nitrosyls. It can undergo different N–O bond cleavage reactions under mild conditions, following reaction with CN^tBu or photochemical decarbonylation. [3] Another NO bridged complex was synthesized from cation **2**, upon reaction with nitrite, to give the trinitrosyl complex $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}NO)(NO)_2]$, where the bridging NO ligand displays a significant pyramidalization at the N atom. This complex can also undergo different NO bond cleavage reactions under mild conditions, following reaction with Zn(Hg) or $P(OEt)_3$.[4]

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PO-7: Synthesis and Characterization of New Chiral Ferrocenylphosphine-Aminoacid Ligands for Aqueous Asymmetric Catalysis

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Keywords: (Asymmetric catalysis, organometallic synthesis, chiral ligands)

Ferrocenylphospine-type ligands emerge as an interesting alternative for the aqueous asymmetric catalysis due to their capacity to include several functional groups to the ferrocenyl backbone, including polar groups to increase their interaction with greener solvents.[1] Different polar groups have been successfully coupled to the ferrocenyl backbone, with excellent catalytic results,[2] however, little information about polar asymmetric ferrocenylphosphine ligands can be found in literature. For this purpose, amino acids appear to be an excellent and group of interest since, coupled to the metallocene fragment, they can increase the solubility of the catalytic system in water, also inducing chirality to a desired product due to the presence of chiral carbons in their structure. In addition, their most attractive quality lies in their enantiomerically pure availability, which makes them an economically accessible fragment by avoiding stereospecific synthetic processes or separations of racemic mixtures. Herein, we proposed a new synthetic approach for the obtention of 4 new water-soluble ferrocenylphosphine-aminoacid ligands of the general formular (S)-(η5-C5H4-PR2)Fe(η5-C5H4-AA) (R= Ph, Cy. AA= L-Pro-OMe, L-Glu-OMe2) for aqueous asymmetric catalysis (Figure1)[3]:

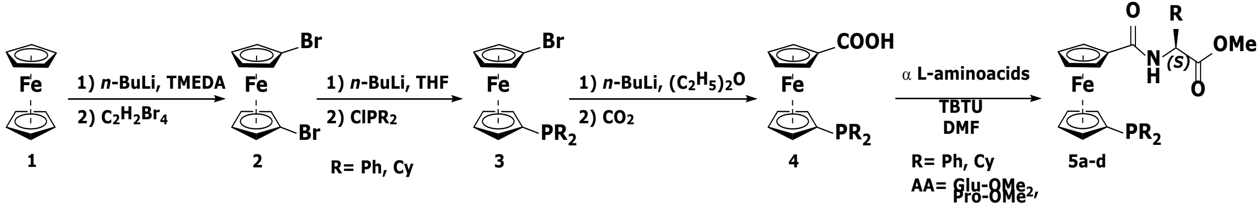

Figure 1. New synthetic route for the synthesis of the ferrocenylphosphine-aminoacid ligands.

Through this route, using economically accessible reagents, 4 new ferrocenylphosphine-aminoacid ligands have been synthetized (**5a-d**) with excellent yields and fully characterized by RMN (^{1}H, ^{31}P, $^{!3}$C). Posterior coordinative and catalytic evaluations of the synthetized ligands will be carried for the aqueous asymmetric catalysis of prochiral olefins under green conditions.

Acknowledgments: A. Teran thanks to ANID Beca de Doctorado Nacional, File 21210985.

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PO-8: Electrochemiluminescence Biosensor for Detecting Single Point Mutation of the KRAS Gene on Screen-Printed Electrodes

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Keywords: Endonuclease, Electrochemiluminescence, KRAS mutation, Screen-printed electrodes

Mutation in the KRAS oncogene is one of the earliest genetic alterations in colorectal cancer (CRC), and it has been recognized as a critical determinant of the therapeutic response of CRC patients. Consequently, reliable and straightforward detection of mutations of this oncogene is of paramount importance for CRC personalized medicine [1,2]. With this in mind, we are developing an electrochemiluminescent (ECL) biosensor on screen-printed carbon electrodes (SPCE) modified with streptavidin to detect a single-point mutation of the KRAS G12D gene. Carboxylic acids were generated on the graphitic surface of the SPCEs via electrochemical oxidation to immobilize streptavidin covalently. Furthermore, the oxidation process was characterized by Raman spectroscopy and X-ray photoelectron spectroscopy. In addition, a biotinylated capture oligonucleotide was immobilized on the biosensor surface. After target recognition by the hybridization reaction, an endonuclease enzyme could recognize and cleave non-perfectly matched DNA. Finally, tris(2,2′bipyridyl)dichlororuthenium(II) intercalated in the double helix and tripropylamine as coreactant were used as ECL probes to recognize hybridization and cleavage events. The platform based on disposable SPCE and ECL as an ultrasensitive technique shows potential for detecting mutated KRAS associated with cancer.

Acknowledgments: The work has been funded by MINCIENCIAS, MINEDUCACIÓN, MINCIT and ICETEX through the Program Ecosistema Científico Cod. FP44842-211-2018, project number 58536, and Ministerio de Innovación y Ciencia- Spain PID2021-123183OB-I00.

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PO-9: Identification of Organic Biomarkers in Ancient Pottery

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Keywords: biomarkers, pottery, ancient

Pottery uses increased widely in the Neolithic age due to the beginning of the sedentary lifestyle. The study of ceramic artifacts can provide us evidence about society structure, diet and economy [1]. Owing to their porous structure, organic compounds can be retained and maintained in the ceramic pottery for years [2]. In the last decades, organic residue analysis have been carried out to identify cooked, consumed or stored food in vessels. These analyses look for persistent and hydrophobic compounds, such as lipids, which are the most common analytes found in ancient ceramics [3]. Compounds as fatty acids can help to identify fats, both animal and vegetal. However, other organic compounds can be used to identify wine (tartaric, succinic, fumaric acid)[4], waxes (*n*-alkanes, alcohols, esters) [5] or opium (alkaloids). This work presents the results obtained from the study of different samples of ceramic pottery from different archaeological sites such as, Castillo de Irulegi, Navarra and Aiatzio, Esnaurreta and Argabi in Sierra de Aralar, Gipuzkoa. These samples had been analyzed by a gas chromatography coupled to mass spectrometry technique, after a one-step ultrasound extraction and hydrolysis, in order to identify wine, milk, fats (vegetal and animal fats), wax, resin, boiling ceramics and opium biomarkers. All the analytes had been qualified through an own library created with the mass spectrums of the compounds of interest. In conclusion, this method allows the identification of various biomarkers of interest to found information about the uses of the ceramics. It is noted that some ceramics were used for different purposes such as storage or for illumination. A larger library is needed to identify more food products or utilities.

Acknowledgments: Alava Central Service of Analysis of SGIker (UPV/EHU, MINECO, GV/EJ, ERDF, and ESF) Basque Country,Basque Government. Project No. IT925-16

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PO-10: Comparison of the use of Phosphorus as an Endogenous Marker in Single Cell Analysis With the use of an Iridium Intercalator for Inductively Coupled Plasma Mass-Spectrometry (ICP-MS) Measurement

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Keywords: single cell, iridium intercalator, ICP-MS, phosphorous, cell marker

In single-cell ICP-MS (inductively coupled plasma-mass spectrometry) studies, phosphorus is an element that is often used as an internal cellular marker due to its presence in all cells as a constitutive element of different cellular components, such as DNA, RNA, phospholipids present in the cell wall, etc [1]. However, measuring this element by single-cell ICP-MS is challenging due to both the polyatomic interferences and the high background given by phosphate buffers used in most biological protocols. This problem has prompted the search for different elements as cell markers. Other constitutive elements, such as iron or copper, suffer from similar problems. But the use of external cell markers, mainly based on heavy metals, is growing due to the highly sensitive detection by ICP-MS with low biological and environmental backgrounds.

In this work, we study the use of an iridium compound as a cell marker for single-cell ICP-MS. This compound is a cationic nucleic acid intercalator containing iridium with a natural isotope composition (^{191}Ir and ^{193}Ir). When the cells are treated with this compound, it intercalates within the cellular nucleic acid, and the detection of both stable isotopes allows the identification of the nucleated cells. For this purpose, the iridium cationic intercalator will be added to human ovarian cancer A2780 cells, which have been previously fixed and permeabilized. The detection of cells using either phosphorus or the iridium as a cell marker will be compared. The iridium labelling of cells will be quantitatively characterized in comparison with the content of phosphorus in the individual cells, with a focus on the intercellular variability.

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PO-11: Exploring the Rigidity of Acyclic Systems for the Complexation of Large Ions With Potential Application in Radiotherapy

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Keywords: coordination chemistry, radiopharmaceuticals, radioimmunotherapy, radiometals

One of the current challenges in cancer treatment is to design treatment and diagnostic methods with a higher degree of specificity. Radioimmunotherapy is a highly specific method based on the conjugation of radionuclide coordination compounds to a biovector with selective affinity for cancer cells. For the preparation of these radiopharmaceuticals, cyclic or acyclic polydentate ligands can be used as bifunctional chelates, although the coordination properties of the current comercial ligands are far from optimal.In this work, two rigid acyclic ligands **L1** and **L2**, and their corresponding La^{3+} complexes (*Figure 1*) were synthesised and structurally characterised in solution. The NMR spectra of **L2** allowed the identification of a dynamic interconversion equilibrium between two confomers in solution. Through the line shape analysis of the ^{13}C-NMR spectra at different temperatures, it was possible to determine the rate constants of the process for each temperature, as well as the $\Delta H^{\ddagger}$ and the $\Delta S^{\ddagger}$ of the equilibrium. In addition, a thermodynamic study of the ligands and La^{3+} complexes was carried out using potentiometric techniques, thus determining the protonation constants of the ligands and the stability constants of the complexes. Both **La-L1** and **La-L2** have proven to be quite stable at physiological pH, as well as in a wide pH range, which positions them as good candidates for the preparation of radioimmunoconjugates with application in radioimmunotherapy.

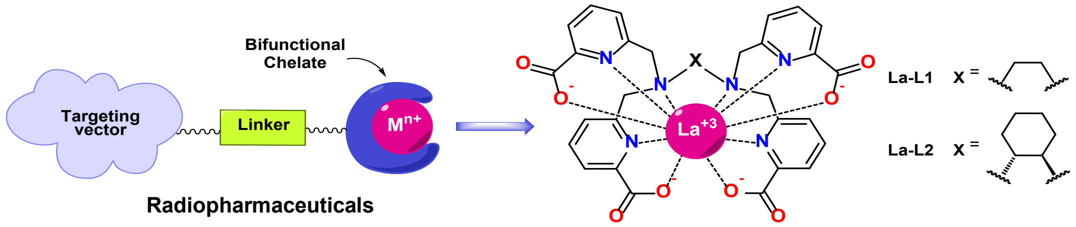

Figure 1: Structure of the complexes presented in this work.

Acknowledgments: Ministerio de Ciencia e Innovación (PID2019-104626GB-I00) and Xunta de Galicia (ED431B-2020/52).

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PO-12: Alzheimer’s Disease Biomarkers Detection Using a Biosensor Based on Novel Magnetic Beads

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Keywords: Magnetic beads, biosensors, Alzheimer’s Disease, Immunosensor

Magnetic beads (MBs) have been notably used as platforms in biosensing thanks to their magnetic behavior as they allow to simplify purification and separation by preconcentrating the sample and minimizing matrix effects, what facilitates the analysis of real samples. Even though it exists a variety of commercially available ones, there is still great interest to develop alternative MBs with improved performance. In this work [1], we propose the synthesis of novel, reliable and low-cost MBs by colloidal assembly of zinc doped magnetite for their use as electrochemical immunosensing platforms. First, zinc doped magnetite ZnxFe3-xO4 nanoparticles (ZnFeNPs) with a diameter of 13 ± 3 nm and a saturation magnetization of 80 emu/g were synthesized and encapsulated in a polymeric matrix of poly(lactic-co-glycolic) acid (PLGA), generating polymeric MBs that were covered with polyethyleneimine (PEI) (MB@PEI), obtaining particles of 96 ± 16 nm. To compare the suitability of the obtained MBs with commercially available ones, the affinity protein neutravidin (NAV) was linked to the MB@PEI. The obtained MB@NAV exhibited a significantly higher saturation magnetization than commercially available NAV-modified MBs, a better reproducibility (RSD of 4% for MB@NAV and 12% for commercial MBs) and enhanced surface functionalization ability when used as immunosensing platforms in a model assay using gold nanoparticle tags. As proof-of-concept, MB@NAV were finally applied for the detection of Tau protein, a well-known Alzheimer’s Disease (AD) biomarker, with a detection limit (LOD) of 63 ng/mL and an excellent performance in human serum samples.

Acknowledgments: We acknowledge MINECO and MICINN (Spain) (CTQ2017–86994-R, MCI-21-PID2020-115204RB-I00, PRE2018-084853 and RyC-2016-20299) and the Asturias Regional Government (FC-GRUPIN-ID/2018/000166).

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PO-13: Femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry as a Powerful Multielemental Direct Solid Microanalysis Technique: Application to Gemstone Analysis

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Keywords: LA-ICP-MS, fs-LA, ICP-TOFMS, gemstones, direct solid analysis

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a well stablished technique for multielemental analysis of solid samples with limits of detection in the order of ppb with low destructive sampling capabilities. In particular, the use of femtosecond pulsed laser ablation systems improves the capabilities of the technique due to less fractionation, and lower matrix-, and thermal- effects [1] leading to more precise results with very low damage done to the sample. Furthermore, novel ablation cell provides ultrafast washouts [2], resulting in very fast ion signals per laser shot. Sequential mass analyzers, such as quadrupole-based or sector field based might suffer from spectral skew problems. Alternatively, Time-of-flight based mass spectrometer (TOFMS) overcome this drawback and allows fast analysis (e.g., fast mapping at high laser repetition rates and fast sample displacement) due to their high mass spectra acquisition rate (> 30 kHz) (e.g. full mass spectrum recording in a few tens of microseconds). In this sense, almost complete elemental coverage with good accuracy can be achieved while producing ultra-low sample damage. These characteristics make fs-LA-ICP-TOFMS an ideal tool to analyze high valuable samples, such as gems or jewelry, or archaeological artifacts where the conservation is a priority. This works aims to improve the measurement conditions (fluence, frequency of the laser, spot size…) and the fs-LA-ICP-TOFMS experimental system response to perform a precise analysis while the damage (ablated material) is minimized.

Acknowledgments:

The authors acknowledge financial support from the Spanish Ministerio de Ciencia e Innovación and the Agencia Estatal de Investigación (Project reference: MCI-21-PID2020-113951GB-I00).

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PO-14: Preparation and Characterization of Sucrose-Based Carbon Foams Loaded with Silver Nanoparticles

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Keywords: carbon foams, sucrose, silver nanoparticles

Carbon materials are very valuable tools for an extensive range of uses. Among them, macroporous carbon foams (CF) appear as very versatile materials for a wide variety of applications such as adsorption, catalysis, thermal and acoustic insulation or electrode manufacturing [1] [2].

This work focuses on the preparation and characterization of CF using sucrose as precursor (SF), which is a very appropriate option for an environmentally friendly CF making. SF were prepared with silver nanoparticles on their surface (SF(Ag)), to be evaluated for different applications. The facile preparation method was intended to be sustainable and cost-effective, and it involves the use of the minimum non-toxic reagents.

To obtain SF(Ag) foams, sucrose was added to a solution of silver nitrate and citric acid. Silver nitrate acts as the source of silver nanoparticles and as foaming agent. The preparation method consisted in three steps. The first was the obtaining of the plastic resin at 80 ºC, the second the preparation of the "green foam" in air using a heating program up to 170 ºC and the final, the carbonization of the green foam under Ar at 900 ºC.

SF(Ag) were characterized by SEM/EDX, nitrogen adsorption, helium and mercury porosimetry and XRD allowing to identify the textural and morphological characteristics of the foam, as well as the size and distribution of the silver nanoparticles on the surface.

Acknowledgments: the authors acknowledge the funding of the work through the research projects PID2020-113558RB-C43 (MCIN/ AEI/10.13039/501100011033) and IDI/2021/000031.

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PO-15: Determination of Betaine, Choline, and Trimethylamine N-Oxide in Serum by Isotope Dilution and 2D-HPLC-ESI-MS/MS

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Keywords: biomarkers, stroke, 2D-UHPLC, electrospray, isotopic dilution.

According to data provided by the World Health Organization, stroke is the second cause of death in the Spanish population. Healthy lifestyle habits, such as physical exercise and adherence to a Mediterranean diet, have been associated in multiple studies with a lower incidence and mortality from cardiovascular and cerebrovascular diseases [1]. Human serum levels of metabolites of the choline pathway indicate adherence to the Mediterranean diet, which could influence ischemic tolerance. It has recently been shown that high plasma levels of trimethylamine N-oxide, which derive from the metabolism of betaine and choline, are associated with a higher risk of incidence and mortality due to stroke [2],[3]. Conversely, high levels of choline and betaine are associated with decreased cognitive impairment and incidence after stroke [4],[5]. Therefore, it is important to routinely evaluate these biomarkers in patients to prevent the incidence of stroke for which there is still no therapy that allows the recovery of damaged neuronal tissue after a stroke. Among the analytical methods used to determine these metabolites in different biological fluids, liquid chromatography coupled with tandem mass spectrometry (LC/MS-MS) stands out. In this work, it is proposed to combine two-dimensional liquid chromatography in the "Multiple heart cutting" mode by combining a reverse phase separation in the first dimension with a cation exchange separation in the second dimension to minimize ionization in the electrospray source. The quantification will be carried out by isotope dilution and the validation of the methodology will be carried out following the CLSI (Clinical and Laboratory Standards Institute) guidelines. The method has been fully validated for lower limit of quantification, linearity, intra- and inter-day precision. Excellent recoveries were observed for betaine, choline, and trimethylamine N-oxide of 96-101%, 95104% and 100-104%, respectively for 9 different concentration levels.

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PO-16: *Ganoderma* aff. *Austral*, a Potential Source of Polysaccharides with in Vitro Antioxidant and Anticancer Capacity

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Keywords: *Ganoderma* aff. *australe*¸ mushroom, polysaccharides.

Mushrooms are widely cultivated worldwide due to their high nutritional value and medicinal properties, since its consumption has been shown to help prevent different types of cancer and heart disease, among other. Mushroom polysaccharides form a major class of bioactive compounds with a wide range of biological activities, including antioxidant, antitumor, and immunological activities. The fruiting bodies of mushrooms represent an important source of biologically active polysaccharides [1.3]. In this context, water-soluble polysaccharides extract from fruiting bodies of *Ganoderma* aff. *australe* (GACP) demonstrated antioxidant and anticancer capacity. GACP was characterized by different spectroscopy techniques. Antioxidant activity was measured by hydroxyl radical, superoxide radical, reducing power tests and lipid model in methyl linoleate. Anticancer capacity was determined in osteosarcoma human cell lines. Chemical characterization indicated that GACP consisted of β-D-Glcp-(1→, →3)-β-D-Glcp-(1→ and α-D-Glcp-(1→ residues. The results of the antioxidant activity showed high antioxidant capacity, and the extract inhibited cell viability and cell proliferation on MG-63 cells. This work demonstrated the bioprospecting of mushrooms is ideal for the isolation of polysaccharides with relevant biological activities in the prevention and treatment of some diseases.

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PO-17: Artificial Neural Networks for the Resolution of Acetaminophen, Ascorbic Acid and Uric Acid using an Array of Sensors of Mesoporous Carbon and Metallic Nanoparticles

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Keywords: electronic tongue; nanomaterials; acetaminophen; ascorbic acid; uric acid.

Electrochemical sensors provide a response to the growing demand of fast and cost-effective analytical methods that allow the on-site detection of relevant analytes in sectors such as clinical, food, industrial, environmental, and forensic chemistry. Unfortunately, few chemical (bio)sensors available can function without interferences or matrix effects. The simultaneous analysis of several compounds in complex samples, with overlapping peaks at similar potentials, may hinder their individual quantification.

In order to improve their analytical properties, the incorporation of nanomaterials has emerged as a promising approach. Therefore, the integration of chemically functional nanomaterials allow the construction of more sensitive, stable, robust, and selective sensors and (bio)sensors. Additionally, to overcome the interferences and signal overlappings, new strategies, such as electronic tongues (ETs) [1], [2], have been developed in recent years.

In this context, the present work aims to demonstrate the potential of metallic nanoparticles (M-NPs) as electro catalysts incorporated into mesoporous carbon (MC) [3], [4]. An array of three sensors modified with gold, palladium, and copper nanoparticles into MC was prepared for the simultaneous resolution of three pharmaceutical compounds of interest: acetaminophen, ascorbic acid, and uric acid. Firstly, voltammetric responses of the sensors were individually characterized for each of the compounds. Next, voltammetric responses of the mixtures were processed with chemometric tools, such as principal component analysis (PCA) and artificial neural networks (ANNs), to achieve the simultaneous determination of the three analytes.

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PO-18: Triorganoindium Reagents in Organic Synthesis: Pd-Catalyzed Dicarbofunctionalization of Alkenes

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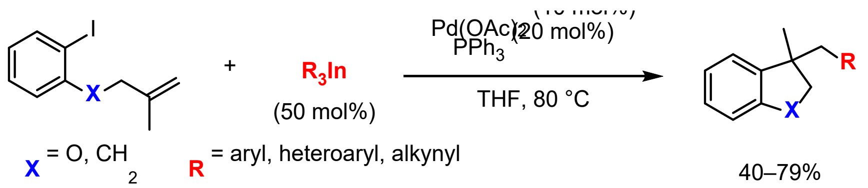
Keywords: Triorganoindium, dicarbofunctionalization, cyclization, cross-coupling.

Indium organometallics are useful reagents in organic synthesis due to their mild reactivity and functional group tolerance.[1] In 1999, our research group discovered that triorganoindium reagents (R_3In) react efficiently with a wide variety of organic electrophiles under palladium catalysis with high atom economy since the three organic groups attached to the indium are efficiently transferred.[2] In this communication we present the novel palladium-catalyzed difunctionalization of alkenes by sequential Heck reaction and cross-coupling using R_3In.

Transition-metal catalyzed alkene dicarbofunctionalization has recently emerged as an attractive and efficient strategy to generate complex structures as two C-C bonds are formed in one synthetic step. The combination of an intramolecular Heck-type cyclization process with a subsequent metal-catalyzed cross-coupling reaction using organometallic reagents represents a direct strategy for olefin dicarbofunctionalization.[3]



In this research, we report that *ortho*-halogenated arenes furnished with an alkene unit react with different R_3In (50 mol%) in the presence of a palladium catalyst to afford the corresponding dicarbofunctionalization products in moderate to good yields. Details about the reaction conditions, scope of the reaction and a mechanistic proposal will be discussed.

Acknowledgments: We are grateful to the Ministerio de Ciencia, Innovación y Universidades (PGC2018-097792-B-I00 and PID2021-122335NB-I00), Xunta de Galicia (GRC2018/039 and GRC2022/039) and EDRF funds for financial support.

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PO-19: Characterization of Waste Cooking Oil Collected in Asturias and Evaluation of its Different Potential Applications in the Plastic Industry

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Keywords: waste cooking oil, sustainability, plastic, chemical characterization, application

Waste vegetable cooking oil (WVCO) is mainly obtained from the food-manufacturing industry, including restaurants and other catering companies. Currently, the production of WVCO in the European Union and United Kingdom is estimated at 0.7 - 1.2 million tons per year, and it is expected that this number will be increased to 1.7 in 2030. Oily waste streams are not easily degradable and can cause a wide range of undesirable environmental outcomes. Generally, vegetable oils are subjected to a series of heating cycles under oxygen exposure and in contact with foodstuff with a certain degree of humidity, which significantly impact their physical-chemical properties. The degree and number of these alterations can vary the range of applications suitable for this residue.

Taking this into consideration, the aim of the current study is to characterize several batches of waste cooking oil gently donated by a local company in Asturias (Aceites Recinorte S.L.), and subsequently evaluate their potential applications for the plastic industry depending on their physical and chemical characteristics. The analytical methods carried out to characterize this WVCO were based on international ISO standards, and the parameters tested were acidity, free fatty acids content, fatty acid composition, peroxide value, moisture content and elemental analysis. Therefore, through the assessment of indexed bibliographic sources, the main characteristics of the analysed WVCO have been related with different applications.

The obtained mean values for the analysed WVCO indicates that it could be used as a chemical platform to produce sustainable plasticizers and compatibilizers to improve ductility and processability in bio-based films for food industry. Additionally, it was observed that it is a suitable carbon substrate to include in bioprocesses owed to produce polyhydroxyalkanoates, a bio-based, biodegradable, biocompatible and with plastic mechanical properties polymer.

Acknowledgments: This study was supported by the Foundation for the Promotion of Applied Scientific Research and Technology in Asturias (FICYT) through the project AYUD/2021/57459.

PO-20: Development of an Alternative GC-C-IRMS Procedure for the Measurement Of $\delta^{13}C$ of Amino Acids from Bone Collagen in Paleodiet Studies

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Keywords: Isotope Ratios, Archaeology, $\delta^{13}C$, Paleodiets, GC-C-IRMS

Stable isotope studies as a tool to reconstruct the diet and/or mobility of populations are increasingly used in archaeological research. It has been indicated that the carbon isotopic composition of amino acids in bone collagen indicate the type of diet of the individuals in the last few years before dead [1]. So far, several studies have been done by measuring the $\delta^{13}C$ in total collagen by converting it to CO_2 and measuring their carbon isotopic composition in a continuous flow isotope ratio mass spectrometer (IRMS) [1]. Such studies provide limited information as the isotopic composition of individual amino acids will be much more informative. For that purpose, the combination of Gas Chromatography with Isotope Ratio Mass Spectrometry would be the ideal choice. However, partial chromatographic overlap is not acceptable in current GC-IRMS instrumentation and software making this application difficult. In this work we have developed and evaluated a new calculation methodology [2], which yields correct $\delta^{13}C$ values even though the chromatographic peaks are not resolved to baseline. As we apply this new methodology, we are improving, optimising some parameters, and improving the interpretation of the results. The procedure was evaluated with certified reference materials and applied to amino acids extracted from the collagen of the bones of skeletons found in medieval cemeteries located in the surroundings of Évora (Portugal).

So, in this paper we investigate the Christian conquest of the city of Évora, in southern Portugal, which was a period of important cultural, religious, and ideological changes. Because of these changes, the population underwent modifications in their diet, leading to differences in the carbon 13 ($\delta^{13}C$) deltas of the collagen present in their bones [1]. For the study, 20 amino acid standards and 63 samples were measured.

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PO-21: Sucrose Foams for Soil Remediation

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Keywords: carbon foams, soil remediation, heavy metals, metalloids, chemical stabilization

Soil degradation is one of the biggest environmental concerns. Among other contaminants, heavy metals and metalloids are the most persistent and challenging to remediate. Therefore, soil remediation strategies based on their immobilization by chemical stabilization have been proposed worldwide [1]. Those approaches often fall under the label of Nature-Based Solutions (NBS) due to the use of sustainable materials and *in-situ* treatment of soils [2]. However, some of the proposed amendments also lead to mobilization of other metal(loid)s, such as arsenic, increasing their availability in the soil.The aim of this study is to evaluate the feasibility of carbon foams obtained from sucrose for remediation of soil contaminated with several metal(loid)s. In order to optimise the properties of these carbon materials, they were impregnated with different concentrations of goethite (FeO(OH)) nanoparticles. Then, soil was incubated with 10% and 20% dose of these carbon foams in a laboratory-scale experiment. Toxicity Characteristic Leaching Procedure [3] and Tessier's sequential extraction [4] were used to determine the availability and mobility of the contaminants. Results have shown downward tendencies in the availability of arsenic, copper, and lead, with some differences depending on the dosage and concentration of goethite nanoparticles.

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PO-22: Novel Analytical Methodologies Based on Elemental Mass Spectrometry for Trace Element and Specific Biomolecule Determination in Extracellular Vesicles Secreted by Human RPE Cells

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Keywords: Extracellular Vesicles, Human Retinal Pigment Epithelial Cells, Single Cell ICPMS.

Age-related macular degeneration (AMD) is a neurodegenerative ocular disease that affects almost 200 million people worldwide and can lead to irreversible blindness. Previous studies of AMD have revealed that progressive degeneration of the retinal pigment epithelial (RPE) cells can play an important role in the development of AMD. As well as mostly all cells, human RPE cells secrete extracellular vesicles (EVs), whose cell-to-cell signalling function may be crucial during early stages of AMD. EVs are membranous vesicles that contain protein and nucleic acid cargo and have gained interest in biomedical research, as they can be potential diagnostic biomarkers. The main aim of this work is to study the possible implication of metal dyshomeostasis in AMD progression through secretory activity of RPE cells. For such purpose, the determination of trace metals concentration in EVs from an *in vitro* model of human RPE cells (hRPEsv40) was performed in both control and pro-oxidative stress treatment conditions by elemental mass spectrometry (ICP-MS). Two isolation strategies of EVs from cell culture medium were evaluated and the thorough characterization of the purified EVs was performed by nanoparticle tracking analysis, transmission electron microscopy and western blot. Considering the limited sample volume available (less than 100 µL), three different introduction systems for microsamples were evaluated to obtain metals concentration in purified EVs. EVs analysed by conventional nebulization ICP-MS provide information of the whole population as an average. However, it is well-known that cell populations in all biological systems have a heterogeneous nature and, therefore, EVs can also exhibit a nonhomogeneous behaviour. Therefore, the combination of single cell (sc) ICP-MS with an immunocytochemistry step using metal nanoclusters as elemental labels has been explored to identify individual EVs purified from control and treated individual hRPEsv cells.

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PO-23: Gas Chromatography-Combustion-Mass Spectrometry, a Powerful Tool to Simultaneous Universal and Quantitative Elemental Detection

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Keywords: Gas chromatography; Mass spectrometry; Selective detector; compound independent quantification

Mass spectrometry has established as one of the most universal and useful detector in gas chromatography due to its capacity to provide universal detection together with structural identification and compound-specific detection (SIM mode). Unfortunately, the structuraldependent signal makes it essential to resort to species-specific standards for quantification. Additionally, identification of specific families of compounds (N, S or O) in complex matrix is very limited being mandatory the use of selective detectors (SCD and NCD) for their detection and quantification. The GC-combustion-MS system presented in 2010[1] allows to provide generic universal quantification of organic compounds while maintaining the structural elucidation capabilities of MS. A combustion interface installed between the column and the MS enabled to convert the organic compounds (containing C) eluting from the column into CO_2 quantitatively. Notably, the most important heteroatoms potentially present in organic molecules (H, N, S) could be detected as well by their corresponding volatile oxide species (H_2O, NO and SO_2).[2] Therefore, it can be considered as the first instrumental system that enables online and simultaneously ultrasensitive elemental quantification, both universal (C, H) and family-specific (N, S), of individual organic compounds eluting from the GC column. The novel set-up consisted of a ceramic tube (400x3x0.5 mm) with 2 Pt wires located inside of a combustion oven and a two position 6-way valve. The online combustion process takes places inside the ceramic tube reactor at temperatures ranging from 850 to 1150 ºC after mixing the elute of the column with an online flow of He:O_2. The conversion of all the eluted compounds to the same volatile species (CO_2, H_2O, NO and SO_2) prior to MS detection enables complete compound-independent quantification opening the door to the use of simple, cheap and certified generic standards. LODs in ppb level or below are within reach for each target elements (C, S, N, H). The robustness of the approach was validated by the analysis of complex real samples.

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PO-24: New Methodology for Doping Smectites with Fatty Acids and for their Spectroscopic Analysis Using Mars Exploration Techniques

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Keywords: Clay minerals, Fatty acids, Spectroscopic Analytical Techniques, Geochemistry

The presence of organic matter in sediments/soils on Mars was revealed by the Curiosity rover, which also detected smectite clay minerals [1]. The most remarkable feature of smectites is their ability to absorb different compounds such as water, cations or organic molecules in the interlayers of their structure [2]. Considering this, the aim of this work is to propose a methodology by which fatty acids, detected on Mars, can be absorbed by smectites and to demonstrate how these compounds can be protected from the ultraviolet radiation present in Mars. Later, the created samples were analyzed by spectroscopic techniques that were or are now being used on Mars, such as X-ray diffraction (XRD), Visible and Infrared (VNIR), and Raman spectroscopies. The procedure began with the smectite activation with H_2SO_4 2M (1:3), which removed the cations from the interlayers and increased the overall negative charge [3]. The reaction was performed in a Parr acid digestion vessel (Parr 4748) where temperature was controlled (90ºC, 4h), at constant stirring (50 rpm). Then, the mixture was filtered and the solid was brought to dryness (60ºC, 72h). Subsequently, the fatty acid solution (60 ethanol) had to react with the activated smectite. To do so, 2 aliquots of activated smectite with fatty acid (5:1) were prepared and the pH was adjusted to 3.3 and 7.3, respectively. Finally, the mixture was agitated in a shaker bath (60ºC, 2h), filtrated and the solid was brought to dryness (60ºC, 24h). The first step to check the methodology was to perform XRD measurements. If the results were successful, Raman and VNIR measurements were carried out. This methodology provides a useful database for current and future in situ measurement missions in Mars and can provide valuable information about how fatty acids could be preserved in Martian soil.

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PO-25: Development Of Multiplatform Strategy For Untargeted Metabolomic Studies In Human Serum By High Resolution Mass Spectrometry

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Keywords: Untargeted metabolomic, high resolution mass spectrometry, methodological development.

Glaucoma is a complex group of eye diseases causing progressive vision loss and consequent irreversible blindness. The clinical diagnosis of glaucoma usually occurs late, by which time up to 30% of vision may be lost, requiring early diagnosis systems based on the analysis of molecular biomarkers (Fernández-Vega Cueto, et al., 2021). More than 500 different molecules have been identified altered in human glaucoma without transference to clinical practice, requiring a novel integrative approach for the discovery of glaucoma biomarkers. With this aim, we developed a multiplatform strategy based in high resolution mass-spectrometry for the non-targeted metabolomics analysis of serum (Zhang, et al., 2012) from glaucoma patients. Two complementary techniques, consisting of a gas chromatograph coupled to a quadrupole time-of-flight (GC-Q-TOF) and a liquid chromatograph coupled to a quadrupole time-of-flight (LC-Q-TOF), were optimized for the metabolomics fingerprint of serum samples from patients with glaucoma and control subjects. Optimization of the sample preparation and measurement procedure for both GC-Q-TOF and LC-Q-TOF analysis was carried out highlighting the possibility of analysing a greater number of metabolites thanks to the multiplatform approach. The optimal conditions were applied to the analysis of serum samples from control and glaucoma subjects, and proper statistical analysis were used for the identification of altered metabolites at systemic level.

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PO-26: Study of the Retention of Pharmaceutical Compounds of Different Therapeutic Classes in the Filtration Step of Water Samples Analysis

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Keywords: pharmaceutical compounds, filters, LC-MS-MS.

The increase of population and industrial development have produced an increase on the presence of potentially toxic compounds. These compounds are known as contaminants of emerging concern (CEC), among them the pharmaceutical compounds and their metabolites are highly spread [1]. The main sources of their presence in the environment are, firstly wastes from laboratories, hospitals and agriculture, and secondly their excretion one they are used which appears in wastewater. Some of them are not removed in wastewaters treatment plants and consequently they could contaminate superficial waters [2]. During the filtration step there is a risk of losing some analytes which are retained in the filter affecting to the reliability of the method.In this study 5 different filters (PVDF, Nylon, Cellulose, PTFE ULP and PP) were tried in order to evaluate the losses of 58 pharmaceutical compounds (including antibiotics, analgesics, cardiovascular drugs and psychiatric drugs among others) during the filtration step in water samples analysis. The determination of the analytes were conducted using high performance liquid chromatography coupled with tandem mass spectrometry (LC-MS-MS). It was shown that the most appropriate material for these compounds was the cellulose one obtaining good analytic retentions for the majority of pharmaceutical compounds studied.

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PO-27: Direct Determination of Intact Protein Phosphorylation with Element Mass Spectrometry and Generic Standards

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Keywords: protein phosphorylation, ICP-MS, absolute quantification, post-translational modifications

The functions and roles of proteins in biological processes are regulated by post-translational modifications (PTMs), of which phosphorylation is one of the most preponderant. Protein phosphorylation is a reversible and dynamic process in which a phosphate group is incorporated (or removed) into certain amino acid residues, and it is involved in the regulation of protein interactions and the control of protein function in almost every cellular process, such as signal transduction, gene regulation, cell cycle or apoptosis, among others. Consequently, changes in phosphorylation degree are related to the occurrence of many diseases, hence the need for analytical approaches that provide accurate quantification of protein phosphorylation.[1] Most common approaches in phosphoproteins quantification are based on the analysis of their enzymatic digest (bottom-up) by molecular mass spectrometry, ESI-MS. These approaches however provide incomplete PTMs characterization. This is why PTM analysis at the intact protein level (top-down) is preferred nowadays. Top-down proteomic approaches cannot solve though the override of phosphopeptides/proteins ionization by more abundant proteic species, which jeopardizes especially phosphorylation quantification, hindering biological interpretation and computational analysis.[2]Alternatively, elemental mass spectrometry (ICP-MS) can rise above some phosphoproteomics limitations by complementing the information obtained by ESI-MS. Current developments in chromatographic separations together with quantitative methodologies in ICP-MS have resulted in the absolute quantification of phosphoproteins at the intact protein level.[3] Monitoring of the S and P trace in the phosphoproteins separated along a single LC-ICP-MS run enables to determine absolute protein concentration from the experimental S molar amount obtained (prior knowledge of the amino acid sequence) and the corresponding phosphorylation degree (from the molar ratio P/S), simply using generic standards of S an P. High precision and accuracy of the S and P quantified enables discrimination between small variations in phosphorylation degree, essential in the study of phosphorylation dynamics.[4] In this work, ICP-MS has proved its usefulness in the absolute quantification of intact proteins phosphorylation in simple protein mixtures and independently of the phosphoprotein abundance. Robustness and quality of the results obtained without resorting to specific phosphoprotein standards make this analytical platform an asset worth considering for overcoming current challenges in phosphoproteomics.

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PO-28: Diastereoselective Gold-Catalyzed Propargylation of Chromone Derivatives from Propargylsilanes

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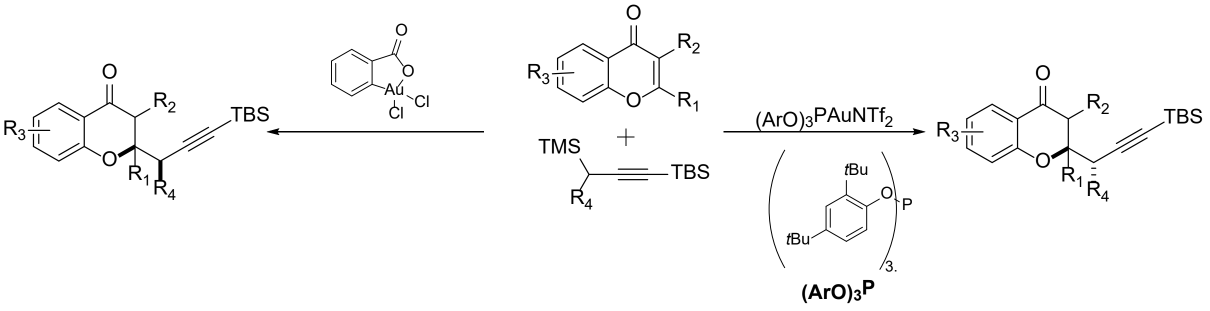
Keywords: Gold, Propargylsilanes, Catalysis, Diastereoselective, Chromone.

The use of gold complexes as catalysts have experienced a big development in the past few years. This has led to the discovery of new and diverse methodologies in organic synthesis for carbon-carbon and carbon-heteroatom bond formation. In this regard, our research group has been focused on studying different types of nucleophilic additions of alkynyl- or propargylsilanes to synergistically activated carbonyl groups.[1],[2] This methodology involves the participation of a σ-allenyl gold intermediate with which has been isolated and characterized.[3] With all this background, we have initiated the study of the gold-catalyzed reaction of different propargylsilanes and chromone derivatives. We chose chromones as the substrate for this transformation because they are natural compounds, can be found in plants, and some of them have been proven to have certain biological activity. Furthermore, they present an α,β-unsaturated carbonyl group in their structure, which means they could function as Michael acceptors. Here we present the first diastereoselective Michael like propargylation of α,β-unsaturated carbonyl groups with propargylsilanes catalyzed by a gold complex. We also discovered that, a change in the nature of the gold complex, can invert the selectivity, making this transformation diastereodivergent.



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PO-29: Photobiocatalytic Linear Cascade for the Stereoselective Transformation of Diazonium Salts into Optically Active 1-Arylpropan-2-ols

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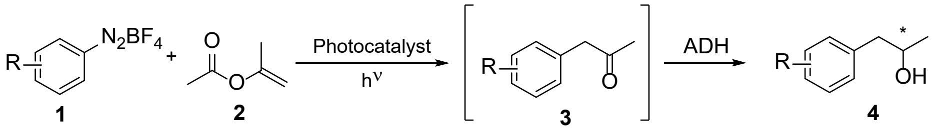
Keywords: Bioreductions; Diazonium salts; Stereoselective synthesis

Photoredox catalysis is nowadays considered a sustainable methodology in organic synthesis through the formation of reactive radical species under mild reaction conditions.[1] In this context, aryldiazonium salts (**1**) are valuable starting materials since they provide access to a broad series of compounds,[2] including 1-arylpropan-2-ones (**3**), reacting with enol acetates, such as isopropenyl acetate (**2**), in the presence, for instance, of tris(bipyridine)ruthenium(II) chloride $[Ru(bpy)_3]Cl_2$.[3] The versatility of these carbonyl compounds has been extensively explored in the literature, finding biocatalytic methods as adequate approaches for the synthesis of the corresponding chiral alcohols using for instance alcohol dehydrogenases (ADHs).[4]

Our objective is to merge photo-and biocatalysis to design a linear cascade, transforming aryldiazonium salts (**1**) in chiral 1-arylpropan-2-ols (**4**) by using stereocomplementary alcohol dehydrogenases (**Scheme 1**).



Scheme 1. Two-step photobiocatalytic sequence towards the synthesis of chiral 1-arylpropan-2-ols.

Suitable reaction conditions will be investigated to combine both steps in one-pot mode, studying the influence of substrate and isopropenyl acetate concentration, type and amount of co-solvent, reaction time, photocatalyst and light irradiation. The substrate scope has been expanded to a representative number of substrates, achieving moderate to good yields and excellent selectivities.

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PO-30: Are The MIL 090030 and the MIL 090136 Paired Meteorites? A Chemical and Mineralogical Assessment

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Keywords: Martian meteorites, paired meteorites, Raman spectroscopy, XRF

When a meteorite crosses the Earth atmosphere, it can be divided in smaller fragments. These fragments can arrive to the Earth surface and they are called paired meteorites [1]. To identify if two or more meteorites are paired, different types of information are necessary, for example, the information about the location in the Earth surface of the different samples or macro-scale analysis [2]. Furthermore, a chemical and mineralogical study of the meteorites can be made. In this work, this type of analysis was made using Raman spectroscopy (in single point and spectral imaging modes) and Energy Dispersive X-Ray Fluorescence, to determine if the Miller Range 090030 (MIL 090030) and the Miller Range 090136 (MIL 090136) are paired meteorites. Both matrixes are formed by pyroxenes (the main mineral), olivines and magnetites. Besides, other minor minerals were found in both meteorites, such us apatite, jarosite or rasvumite. In addition, different types of SiO2 polymorphs were found instead of quartz because of the high temperatures and pressures suffered by the meteorite. Both meteorites were found in the Antarctica, which explains the presence of some alteration minerals as calcium sulphates, nitrates, halite and goethite due to the weathering environment of this region. Considering the similarities in the chemical and mineralogical composition between the MIL 090030 and MIL 090136 Martian meteorites, it can be stated that both are paired meteorites.

Acknowledgments: All the authors are grateful to NASA for accessing to the MIL 090030 and MIL 090136 Martian meteorites. US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center. This work has been supported through the RamanOnMars project (Grant No. PID2019-107442RB-C31, funded by the Spanish Ministry of Science and Innovation, and the European Regional Development Fund), and the Strategic Project ''Terrestrial and Planetary Alteration Processes'' (Grant No. UPV/EHU PES21/88), funded by the University of the Basque Country (UPV/EHU). J. Aramendia is grateful to the UPV/EHU and the Ministerio de Universidades for her post-doctoral Maria Zambrano position.

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PO-31: Virtual Screening of Novel Asymmetric Phenethylamines Obtained by Chiral Lithium Amides

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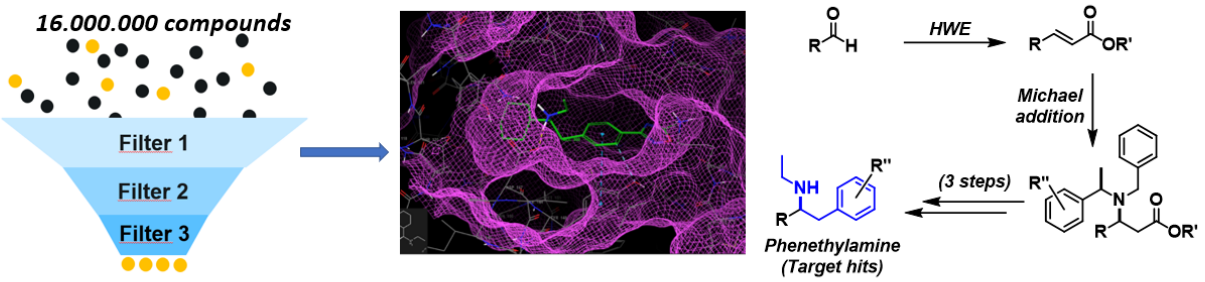
Keywords: Phenethylamines, opioid receptors, virtual screening, molecular docking.

Phenethylamines are relevant compounds known to interact with key neuroreceptors as the opioid, adrenergic or 5-HT families.37 years ago, several simple phenethylamines were developed as novel analgesics targeting opioids receptors.*(1)* Since then, the research around these motifs and their corresponding chemical space has been scarce, avoiding the possibility of emergence of a new potential group of analgesic drugs. We present here a rational VS (virtual screening) campaign of asymmetric phenethylamines to furnish innovative chemical space with analgesic properties. To carry it out, a focused library based on the methodology employed for the synthesis of these asymmetric phenethylamines has been constructed, containing more than 16.000.000 compounds. A series of filters, like physchem properties and molecular docking, were used to achieve a high-valuable phenethylamine space with promising molecular properties towards opioid receptors agonism. These hits were materialized in the lab using a 5-step asymmetric synthesis described previously.*(2)*



Virtual screening workflow ***Molecular docking*** ***Asymmetric synthesis***

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PO-32: Chemoenzymatic Synthesis of Optically Active Aliphatic Halohydrins Combining the use of Gold(I) Species and Alcohol Dehydrogenases

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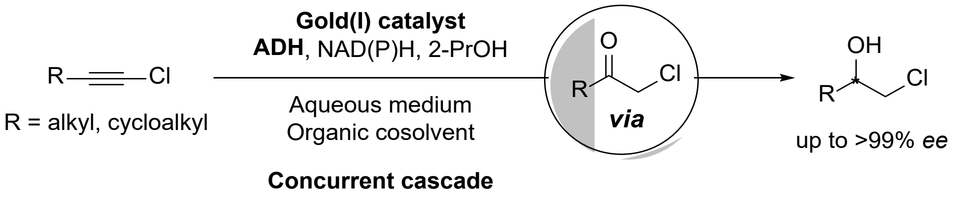
Keywords: alcohol dehydrogenases, aliphatic halohydrins, alkynes, cascade, gold(I) catalysis

Chiral halohydrin derivatives are versatile intermediates in organic chemistry, as they can be easily functionalised to provide several families of biologically active compounds and synthetic drugs.[1] Traditionally, these compounds have been synthesized through (bio)reduction of α-halomethyl ketones under asymmetric hydrogen transfer conditions using chemical catalysts or alcohol dehydrogenases (ADHs).[2] Since this transformation is highly thermodynamically favoured, only a little excess of the hydrogen donor (e.g. 2-propanol, 2-PrOH)[3] is required, which acts as a co-substrate, but also for NAD(P)H cofactor recycling purposes in the case of reactions mediated by ADHs. The synthesis of aliphatic halohydrins is particularly challenging because chemical halogenation reactions to obtain the corresponding α-haloketone precursors usually occur in a non-selective fashion.To circumvent this problem, haloalkynes appear as ideal carbonyl surrogates, since they are easily accessible. Thus, the preparation of the corresponding α-halomethyl ketones via regioselective hydration of haloalkynes can be considered as a direct and atomically efficient synthetic approach.[4] Gold(I) catalysts have recently emerged as valuable tools for the hydration of alkynes, so based on our experience in the combination of N-heterocyclic carbenes (NHC)-Au(I) and ADHs,[5] herein we propose the stereoselective synthesis of a series of aliphatic halohydrins from haloalkynes via concomitant alkyne hydration and biocatalytic bioreduction sequence in order to obtain the desired products with good yields and stereoselectivities



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PO-33: New Approach to the Synthesis of Spirocyclic Lactones by Transition Metal-Free Reactions of *N*-Tosylhydrazones and Boronic Acids

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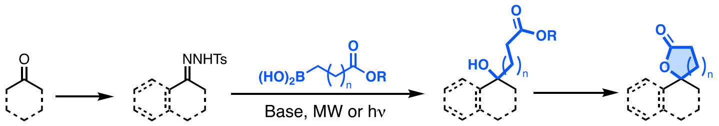
Keywords: *N*-Tosylhydrazones, boronic acids, transition metal-free, spirolactones.

Spirocyclic moieties are very appealing in medicinal chemistry, as the rigid three-dimensional structure of the sp^3-rich scaffold orients the substituents towards different directions, allowing the exploration of new areas of the chemical space in drug discovery programs. Spirolactone moiety, in particular, has been recognized in a wide array of natural and non-natural scaffolds showing a variety of useful pharmacological properties [1]. For these reasons, the development of new methodologies oriented to the synthesis of structurally diverse spirolactones are a goal of interest in medicinal chemistry. The transition metal-free reaction between *N*-sulfonylhydrazones and boronic acids first reported by our group [2], has found great application in organic synthesis. This reaction proceeds through the carboborylation of the *N*-sulfonylhydrazone to give rise a homologated boronic acid that can undergo protodeboronation or be trapped in a subsequent reaction [3]. Alternatively, this intermediate boronic acid can be oxidized in the reaction conditions or by the addition of hydrogen peroxide. Based on this idea, we envisioned that employing N-sulfonylhydrazones derived from cyclic ketones and boronic acids with an ester funcionality as coupling partners, the access to spirocyclic lactones could be achieved. The reaction between N-tosylhydrazones and boronic acids took place nicely without any transition-metal catalyst under microwave or light activation, and the resulting homologated boronic acid was completely oxidized by the addition of hydrogen peroxide. The subsequent lactonization of the corresponding alcohol was achieved under acidic conditions obtaining the expected spirolactones. Herein, we present a new methodology for the synthesis of spirolactones based on a cross-coupling reaction between N-sulfonylhydrazones derived from cyclic ketones and boronic acids with an ester functionality. The overall process comprises the transformation of carbonyl compounds into spirocyclic lactones with five and six member rings in a transition metal-free process.



- Transition metal-free
- More than 20 examples
- Csp^3-Csp^3 and Csp^3-O bonds formed on the same C
- sp^3 enriched structures

Acknowledgments: PID2019-107580GB-I00/AEI/10.13039/501100011033

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PO-34: Removal of Metals from Aqueous Solutions by Carbon Foams Obtained from Sucrose

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Keywords: sucrose foam, heavy metals, wastewater treatment; iron oxides

Contamination of water by many pollutants, especially heavy metals, poses a serious threat to public health and the environment [1]. Metal ions such as Hg(II), Cu(II), Pb(II) and As(V) are well known for their high toxicity that can cause serious effects on human health (kidney damage, cancer, nervous system damage, etc.) [2]. Several processes and techniques have been developed for the extraction of heavy metals from polluted water such as chemical precipitation, electrochemical methods, ion exchange and adsorption [3]. Various types of materials such as zeolites, clay, mesoporous carbon, metal−organic frameworks (MOFs), etc. [4] have been used for possible removal of toxic ions. However, some of these conventional treatments can generate a large amount of new toxic waste.The objective of this study was to develop a new carbon material based on carbon foam obtained from sucrose to remove heavy metals from aqueous solutions, giving rise to an economically and environmentally sustainable adsorbent.Batch adsorption tests were carried out to evaluate the ability of Fe-impregnated carbon foams to remove As, Se, Hg, Cd, Cu, Pb and Zn from contaminated synthetic water. Batch adsorption tests were performed in 50 mL Falcon tubes using different ranges of carbon foams and contact times. Metal concentrations ranged from 25 to 100 ppm. The results were compared with a commercial activated carbon. The results of this study reflected that the developed carbon foams could be an effective and sustainable method to remove heavy metals from water.

Acknowledgments: This work was funded by the research projects PID2020-113558RB-C43 (MCIN/ AEI/10.13039/501100011033) and IDI/2021/000031. The authors acknowledge Programa Investigo, Mechanism de Recuperación y Resiliscencia for the funding received for the hiring of Lucía López-Toyos.

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PO-35: Study on the Diagnostic Value of lncRNAs as Plasma Biomarkers of Colorectal Cancer

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Keywords: circulating biomarkers, colorectal cancer, early diagnosis, lncRNAs.

Long noncoding RNAs (lncRNAs) constitute a large and scarcely explored class of non-protein coding transcripts, which have emerged as new players in the cancer paradigm [1]. Their dysregulated expression levels in human body fluids accessible have been associated with different types of cancers, thus fuelling the interest in exploiting their clinical potential as minimally invasive cancer biomarkers for liquid biopsy [2]. In the particular case of colorectal cancer (CRC), the determination of aberrant expression of lncRNAs in plasma could become a less risky, painful, and expensive alternative to colonoscopy, the current screening method for CRC early diagnosis [3].

In this work, the expression of 9 lncRNAs was analysed by one-step quantitative reverse transcription PCR (RT-qPCR), using beta-actin as an endogenous control, in the plasma of CRC patients and healthy controls. The recorded data showed the overexpression of 5 lncRNAs in samples positive for colorectal cancer, although their individual diagnostic value is limited. Among all of them, the lncRNA UCA1 stands out with a clinical sensitivity and specificity of 88 and 85%, respectively. The use of chemometric methods such as supervised linear discriminant analysis and artificial neural networks provided panels of 3 lncRNAs that generated classifications of samples with excellent clinical parameters (sensitivity and specificity), comparable to those of colonoscopy.

Acknowledgments: The work has been financially supported by Spanish Government (project PID2021-123183OB-I00).

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PO-36: Selection of Tumour Surface Biomarker Specific Aptamer for Targeted Delivery Nanosystem as Innovative Hepatocellular Carcinoma Treatment

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Keywords: hepatocellular carcinoma; glypican 3; aptamer; SELEX technology; targeted delivery

Hepatocellular carcinoma (HCC) raises many concerns due its increasing incidence, low-sensitivity screening methods and a five-year survival rate of only 18% [1]. Many patients diagnosed at advanced stages or without the possibility of surgical and loco-regional therapies are relying on systemic therapy, which unfortunately possess some drawbacks as systemic adverse effects, low absorption in tumour tissue and drug resistance [2]. Aptamers are short, single-stranded DNA or RNA sequences, obtained *in vitro* through a process called Systemic Evolution of Ligands by Exponential Enrichment (or SELEX). Through target-induced specific 3-D structures they can bind to a wide variety of target molecules with high affinity and specificity. Their improved thermal and chemical stability, low immunogenicity and little to no batch–to–batch variations make them promising candidates for passive targeting elements in the design of targeted drug delivery systems [3]. This poster presents the main strategy for the selection of a new aptamer through magnetic–beads SELEX technology for glypican 3 (GPC–3), an HCC biomarker found on the surface of hepatic tumour cells. Multiple selection rounds are envisioned using different serum proteins as counter molecules to make the selection more stringent, eliminate the major possible interferences and select the aptamer with the highest affinity towards the target. The obtained aptamer will be further explored for its specific recognition and binding abilities for the development of a targeted delivery system based on magnetic nanoparticles functionalized with an antiangiogenic tyrosine kinase inhibitor drug, as a theranostic nanocarrier device that can be guided to the tumour site using a magnetic field for both imaging and drug delivery purposes. The selection of a GPC–3 specific aptamer *via* SELEX technology and its further incorporation into a targeted delivery nanosystem could improve the treatment with tyrosine kinase inhibitors and potentially influence the outcomes of HCC patients.

Acknowledgments: The funds for this work have been obtained from XXX and project PID2021-123183OB-I00) financed by MCIN/AEI/10.13039/501100011033/ FEDER, UE. M. Casian thanks the Iuliu Hațiganu UMF internal grant no. 881/10/12.01.2022.

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PO-37: Protein Extraction from Agar Industry Waste Using Deep Eutectic Liquids

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Keywords: agar industry, deep eutectic solvents, bioactive, proteins, antioxidant

In the agar industry, a lot of wastewaters are generated, which mainly comes from the washing and processing of algae to obtain agar. In this sense, in order to give to these wastewaters a second life, the extraction of their bioactive compounds by using organic solvents has been evaluated by many other researchers. However, organic solvents are pollutants, toxic and inflammable, so the investigation of safe and eco–friendly alternatives is highly encouraged. Among the new generation of green solvents, can be highlighted the deep eutectic solvents, which are solutions of Lewis or Brønsted acids and bases which form a eutectic mixture. Therefore, the main objective of this research work was to evaluate the performance of different deep eutectic liquids when extracting useful bioactive compounds from agar industry wastewaters. In this sense, the optimal methodology to achieve the best efficiency and antioxidant capacity of the extracted compounds was also tested.

For this purpose, a series of extractions were carried out using different eutectic liquids based on chlorine chloride (ChCl) in combination with lactic acid, ethylene glycol and glycerol. According to the results obtained, the solvent formed by ChCl (C1) and lactic acid (C2) is the one that achieves the best performance. Once chosen the best eutectic liquid, the extraction process was optimized varying three variables: reaction temperature, C1/C2 ratio and eutectic solvent/algae residue ratio. The optimum extraction allowed the recovery of 99% of the protein present in the wastewaters and, in addition, the protein recovered showed noticeable antioxidant properties.

Acknowledgments: This study was supported by Roko Industries S.A., which kindly donated the algae treatment residues that allowed this work to be carried out.

PO-38: Study of Atomic Shell Structure Through the Calculation of Maxima of Square of the Wavefunction Using Quantum Monte Carlo

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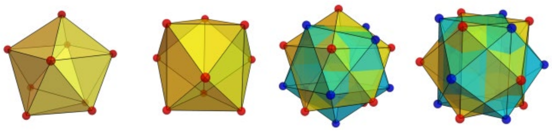
Keywords: Born probabilities, atomic shell structure

Through the study of the maxima of the square of the wavefunction, a comparison of the atomic shell radii for different atoms is provided, in addition to study the persistence in molecular systems and obtaining results that are easily interpretable through chemical intuition. These results are obtained by applying the Quantum Monte Carlo Variational method to systems from H to Kr. The obtained results are compared with other descriptors like the Laplacian of the electron density, the electron localization function (ELF) and the Localized Orbital Locator (LOL). According to Born probabilities, electrons are distributed in semi-spherical shells. The distances of the shells are close to those provided by the density Laplacian and tend to be substantially smaller than those of the ELF or LOL.

One of the most interesting results obtained is the description of the structure of the M shell, where the d orbitals are included. We think that this spatial image should be particularly appealing to the chemist, providing a conceptual framework in which cores and valences are visually identified at a glance.



As for the analysis performed on molecular systems, the atomic shells are distorted when the chemical bond is formed. On the other hand, the use of Born maxima allows to perfectly distinguish the shells that appear merged with other descriptors, in the same way that it is possible to distinguish with the Laplacian analysis.

The study of Born probabilities on atoms provides an alternative shell structure descriptor which we think displays many advantages over other available indices. It considers, in principle, the full N electron correlations, which can lead to sizable effects. In cases in which a neutral maximum (without ionization) exists in molecules, the preservation of the atomic shells is rather impressive.

Acknowledgments: the authors acknowledge the Spanish MICINN for financial support (Grant No. PGC2018-095953-B-I00) and the FICyT (Grant No. IDI-2021-000054). María Menéndez-Herrero specifically acknowledges the Spanish FICyT for the predoctoral grant (No. PA-21-PF-BP20-034).

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PO-39: Synthetic Versatility of Fe(III)-Based Deep Eutectic Solvents (*DES*s), an Active Reaction Media for Meyer-Schuster Rearrangement, Hydration of Alkynes, Formation of C-C Bonds and Oxidation of Thioethers

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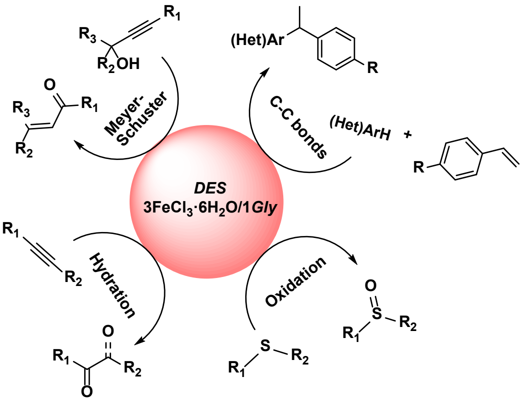
Keywords: metallic catalysis, Deep Eutectic Solvents, alkyne hydration, carbon-carbon bond formation, oxidation.

Deep eutectic solvents (*DES*s) with Brønsted or Lewis acidity are capable of playing a key role in various transformations, such as oxidations, aldol or pericyclic reactions, as well as condensation and multicomponent reactions.[1] In recent years, the interest in *DES* containing metal salts has increased due, principally, to their inherent catalytic and oxidizing properties.

In this sense, our research group has explored the wide synthetic versatility of a Fe(III)-based *DES* ($3\mathrm{FeCl_3}\cdot 6\mathrm{H_2O}/1\mathit{Gly}$) which promotes several catalytic processes such as the Meyer-Schuster rearrangement of alkynols,[2] the hydration of internal and terminal alkyne, the formation of carbon-carbon bonds and the oxidation of tioethers.



Acknowledgments: PA-21-PF-BP20-093; PID2020-113473GB-I00

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PO-40: In Search for Potential Biomarkers, at Elemental and Isotopic Composition Level, for Ocular Neurodegenerative Diseases

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Keywords: Elemental & Isotopic analysis, Age-related macular degeneration, Glaucoma, Multicollector ICP-MS, Sector-field ICP-MS

In a biomedical context, the search of potential non-invasive or minimally invasive biomarkers in biological fluids are of great relevance for the diagnosis/prognosis of diseases, especially for those ones that are only diagnosed at a later stage. Homeostatic elemental compositions of mineral elements present in biological compartments (body fluids and tissues) might be altered during the onset and pathogenesis of a disease and so can be used for the search of biomarkers for a particular disorder. Furthermore, disease conditions may also affect their isotopic composition as a result of the isotope fractionation that accompanies (bio)chemical reactions and (bio)physical processes. So far, blood is the most common fluid investigated for such purposes. Nevertheless, the use of biological fluids directly related to the diseased organ could provide a more reliable information.

In this context, we aim at investigating the potential of elemental and isotopic analysis focusing on ophthalmological disorders, particularly those related to neurodegenerative processes such as glaucoma and age-related macular degeneration (AMD). As a representative example, ionomic variability at elemental and isotopic level, for Cu and Zn (both play an essential role in the visual cycle) [1]) by sector-field ICP-MS and multi-collector ICP-MS in a systemic biological fluid such as serum and an ocular fluid, aqueous humor, will be presented in this work.

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PO-41: Development of a HPLC-ICP-MS Methodology for Stroke Differential Diagnosis in Nasal Exudate

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Keywords: Stoke, nasal exudate, HPLC-ICP-MS

According to The World Health Organization (WHO) the cerebrovascular accident (CVA) or stroke is the second cause of death worldwide. There is also a high morbidity associated with this pathology, about 50% of survivors end up chronically disabled. CVA can be classified as ischemic (caused by a blood clot) or hemorrhagic (produced by broken blood vessels), both causing a decrease in the blood flow to the brain. This organ is highly immunoprotected by the blood-brain barrier, so the access to direct clinical parameters associated with the CVA is rather limited. Therefore, blood tests are typically used to help in the diagnosis (together with head computerized tomography and magnetic resonance imaging for instance). The recent description of a lymphatic drainage from the brain to the nasal mucosa paves the way to investigate nasal exudate to provide information about CVA [1].

In this context and aiming at the search of potential biomarkers for differential diagnosis of CVA, we have investigated the potential differences in the protein profile of Fe and Cu between ischemic and haemorrhagic stroke patients. For such aim, a method based on size exclusion chromatography, SEC-HPLC, coupled to ICP-MS and quantitative analysis via post-column isotope dilution (IDA) has been developed for nasal exudate. Comparison between patients diagnosed with ischemic and hemorrhagic stroke patients and control individuals has been then performed to establish potential alterations in the protein profile.

Acknowledgments:

This work was financially supported through project AYUD/2021/51289 (PCTI Program of the Government of the Principality of Asturias and FEDER Program of the European Union) and PID2020-118376RA-I00/Agencia Estatal de Investigación (AEI)/10.13039/501100011033).

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PO-42: Towards the Development of CB[8]-Based Rotaxanes

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Keywords: Supramolecular chemistry, Rotaxanes, cucurbit[n]urils, DFT-D calculations, isothermal titration calorimetry.

The mechanically interlocked molecules known as rotaxanes, are no longer considered a mere curiosity, as being already implemented in functional systems such as sensors, nanovalves, etc.[1] Following our previous work,[2] we describe herein the first steps towards the development of new [2]-rotaxanes having cucurbit[8]uril (CB[8]) wheels, and axels composed of pyridinium salts stoppered with alkyltriarylphosphonium derivatives. For this purpose, the complexation of CB[8] with a model of recognition station (paraquat, **MV**$^{2+}$) as first guest was studied together with two potential second guests as releasable cargoes: naproxen (**N**) and a 2,6-dihydroxynaphthalene derivative (**A**). Experimental results indicated the possible formation of heteroternary complexes (**MV**$^{2+}$·**A**/**N**$\subset$CB[8]), in agreement with DFT-D calculations, which also provided information on structural differences between the complexes as a function of the protonation state of the second guests (**A**H/**A**$^-$ and **N**H/**N**$^-$). Finally, the study of the complexation with CB[8] of a combined model of the recognition station and an alkyltriarylphosphonium derivative (model B), allowed us to observe the formation of an unusual pseudoheteroternary complex, with $K_a = 3.7 \cdot 10^7$ M^{-1}, considerably high for a binary complex. Likewise, a simplified version of model B, (model C) also showed the formation of a pseudoheteroternary complex ($K_a = 3.2 \cdot 10^7$ M^{-1}).

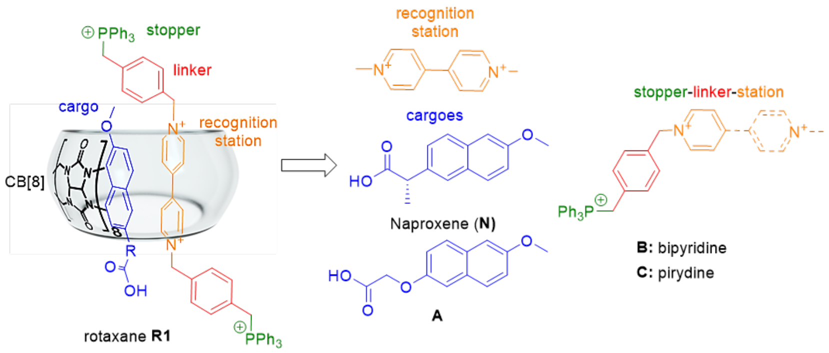

Figure 1. Model components studied for rotaxane **R1.**

Acknowledgments: The authors are grateful for the funding received from the Agencia Estatal de Investigación (PID2019-105272GB-I00), the Consellería de Educación, Universidade e Formación Profesional, Xunta de Galicia (ED431C 2022/39 and 508/2020). M.D.A. thanks Ministerio de Educación y Formación Profesional (FPU program).

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PO-43: NNAIMQ 2.0: A GUI-based Code for the Calculation of Well-Behaved QTAIM Atomic Charges with Neural Network Models

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Keywords: QTAIM, Neural Networks, Atomic charges, Machine Learning

The Quantum Theory of Atoms in Molecules (QTAIM) [1] provides a particularly rigorous way to compute reliable partial charges at the expense of a large computational cost. In this context, we have recently developed NNAIMQ [2] a neural network (NN) model capable of predicting QTAIM charges of C, H, O and N atoms in a fraction of the standard computational time. Unfortunately, the independent nature of the atomistic NN does not guarantee the exact reconstruction of the net molecular charge, something which is crucial for certain applications (e.g estimation of the electrostatic component to the total interaction energy [3]). Trying to ameliorate this problem, in this work we combined the inferring abilities of NN with a charge equilibration strategy that ensures the adequate behavior of the resultant charges. Moreover, this approach has been coupled to a python based GUI which makes the analysis and computation of partial charges much easier and appealing to users outside the computational chemistry community. The performance of the code, referred to as NNAIMQ 2.0, and the different electron redistribution algorithms is put to the test in a variety of scenarios including equilibrium geometries, chemical reactions and large (supramolecular-like) systems. Altogether, the results obtained point out that the corrections imposed by the charge equilibration schemes are, on a general basis, subtle enough to hold the quantitatively and qualitatively quantum chemically accurate trends recovered by the Neural Network models.

Acknowledgments:

M. Gallegos specially acknowledges the Spanish MCIU for a pre-doctoral grant (reference FPU19/02903).

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PO-44: Expanding and Contracting the Dimensions of the "Redbox"

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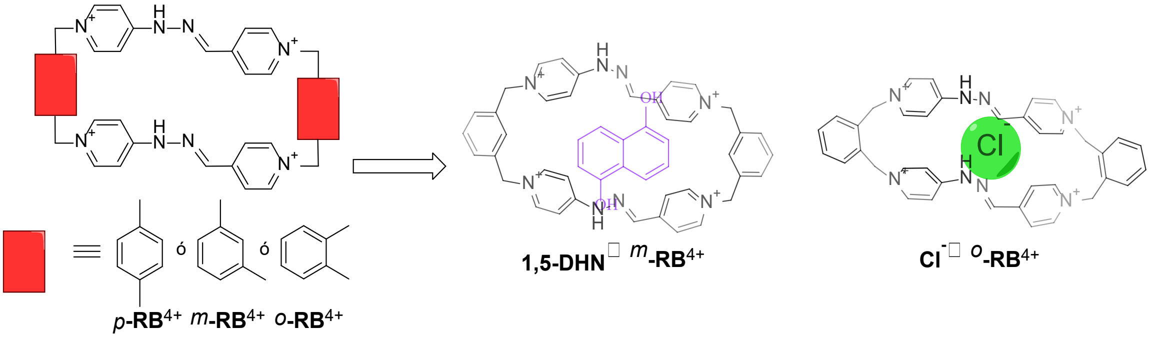
Keywords: Supramolecular chemistry, cyclophanes, molecular sensor, DFT-D calculations.

In recent years, new molecular cationic receptors have been developed[1] implementing diverse functionalities, such as catalyst or sensing.[2] Based on the well-known tetracationic *bluebox* cyclophane, a hydrazone analogue (the *redbox p-**RB**$^{4+}$*), has been recently developed in our group.[3][4] In the work presented herein, we have synthesized two new analogues of the *redbox*, in which the distance between the long sides of the macrocycle is reduced (*meta-redbox m*-**RB^{4+}**, and *ortho-redbox o*-**RB^{4+}**). The cyclophanes have been fully characterized by ^{1}H and ^{13}C NMR and ESI-MS techniques. Experimental results show the existence of diverse stable conformers for *o*-**RB**$^{4+}$, in agreement with DFT-D calculations.

Due to the presence of pyridinium units, *m*-**RB^{4+}** and *o*-**RB^{4+}** could form inclusion complexes with π-donor substrates, such as 1,5-dihydroxynaphthalene (**1,5-DHN**). However, only *m*-**RB^{4+}** was found to form such complexes by having the right cavity size. Moreover, having two hydrazone groups, both macrocycles were found to interact with anions *via* H-bonding through their N-H moieties, as proven by NMR and UV-vis studies with **Cl$^-$**.



Acknowledgments: The authors are grateful for the founding received from the Agencia Estatal de Investigación (PID2019-105272GB-I00), the Consellería de Educación, Universidade e Formación Profesional, Xunta de Galicia (ED431C 2022/39 and 508/2020).

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PO-45: Phenol Red and Malachite Green as Dual Optical/Electrochemical Indicators for Loop-Mediated Isothermal Amplification (LAMP)

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Keywords: Loop-mediated isothermal amplification, electrochemistry, phenol red, malachite green, SARS-CoV-2.

Loop-mediated isothermal amplification (LAMP) is paving the way for simple nucleic acid amplification-based sensing. This technique shows great specificity and sensitivity when compared to well-established techniques. With a single temperature step, this method is an appropriate solution for point-of-care detection of nucleic acids. However, LAMP readouts usually rely on either naked-eye visualization (i.e., colorimetric/fluorometric/turbidimetric changes) or complex instrumental practices that lengthen the workflow and thus hamper its decentralization. For this purpose, electrochemical techniques arise as an alternative for fast quantitative decentralized methodologies.

Most of the approaches for electrochemical LAMP detection are based on strategies with additional reagents and steps, increasing time and cost significantly. In this work, the use of electrochemical probes already included in commercial LAMP kits is presented as a basic approach to obtain quantitative information without further reagents or workflow steps. Phenol red (PR) and malachite green (MG), common colorimetric indicators in LAMP and readily available in many commercial master mixes, also exhibit changes in their electrochemical behavior after LAMP, which could be characterized and correlated to initial DNA/RNA copies. To this end, we have assessed the changes in the electrochemical activity of PR and MG during LAMP: PR reveals an oxidation peak that shifts toward more positive potentials as amplification occurs, while MG shows an oxidation peak whose intensity decreases as LAMP progresses. Based on these changes, two electroanalytical methodologies for SARS-CoV-2 RNA quantification were developed, obtaining limits of detection as low as 21 copies/µL. They were validated with clinical samples as well, demonstrating the applicability of the method.

Acknowledgments: This work has been supported by grant PID2020-118376RA-I00 funded by MCIN/AEI/10.13039/501100011033, grants PID2020-116329GB-C22 and TED2021-129336B-I00 funded by MCIN/AEI/10.13039/501100011033, project AYUD/2021/51289 (Government of the Principality of Asturias, FICYT and FEDER Program of the EU), and project LIFE of Fondo Supera COVID-19 from Banco Santander, CRUE and CSIC.

PO-46: Single Cell Evaluation of Selenium Nanoparticles and Selenized Yeast Extracts Treatment in Ferroptotic Cell Death

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Keywords: selenium, ferroptosis, single cell ICPS-MS

In recent years, an iron-dependent non-apoptotic cell death pathway has been proposed, called ferroptosis, which plays a very important role in a wide variety of diseases. The mechanism of this type of death is associated with an increase in the production and accumulation of reactive oxygen species (ROS) through the Fenton reaction. One characteristic of ferroptosis is the iron-dependent lipid peroxidation, which can be inhibited by the key Se-dependent regulator of ferroptosis glutathione peroxidase 4 (Gpx4), radical-scavenging antioxidants and specific inhibitors of ferroptosis, such as ferrostatins and liproxstatins, as well as iron chelation [1, 2]. Some recent studies show that pharmacological selenium supplementation, even in the absence of nutritional deficiency, has an unexpected ability to drive adaptive transcription to counteract ferroptosis (and other stresses) and specifically protect neurons.

Therefore, in this work we intend to study the protective effect of Se through cell treatments with Se nanoparticles (SeNPs) and yeast extracts rich in this element (SELM-1) after inducing ferroptosis with erastin as a model molecule. For this purpose, commercial SeNPs with an average size of 20 nm were characterized, as well as a Se-enriched selenized yeast extract (SELM-1), using different techniques such as single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) and transmission electron microscopy (TEM). In addition, the toxicity of both these and erastin, as an inducer of apoptosis, was studied in Hep-G2 liver cancer cells. Likewise, the levels of cellular incorporation of Se from the different sources in liver cells were evaluated using single cell ICP-MS strategies. Preliminary results showed a more effective incorporation of Se from the yeast extract than from the synthetic nanoparticles. Also, a monitorization of the presence of ROS and lipid peroxidation in the presence of erastin and erastin + Se was carried out to study the protective effect of this element.

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PO-47: Effects of Pesticides on *Apis Mellifera* Populations

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Keywords: Honeybee, pesticides, pollinators, crops.

Colony Collapse Disorder (CCD) is a phenomenon that occurs when the majority of bees in a honeybee colony, generally worker bees, die out unexpectedly. Because the queen needs the nectar provided by the workers to nurse new bees, finally the entire colony collapse.[1] The latest researches agrees that this phenomenon is not only dependent on an specific pathogen agent, but also in a combined effect of the action of certain pesticides, parasitic diseases like Varroosis, fungus *Nosema*, the loss of natural habits due to the extension of monocultures and climate change.[2] This study focused on the cause-effect relationship between certain pesticides and CCD. Pesticides are used to protect crops from harmful insects and diseases, but the pesticide exposure can be deadly to other animals.[3] When a honeybee pollinates a plant sprayed with pesticides it can easily be contaminated and poison other bees, causing physiological problems and dead. Honeybees are the most important pollinators of many of the fruits and vegetables we eat, that is why there is a need to demonstrate the causes of CCD.[4] In this research It has been monitored a list of pesticides from neonicotinoids, piretroids and sulfoximin families used in several crops like wheat, barley, vineyard, sunflower and rapeseed. In addition, several apiaries in the Álava region close to the aforementioned crops have been selected to collect samples. The main object of study is bees but samples of other beekeeping matrices such as honey, wax or pollen have also been collected. The objective of this research work is to analyse the pesticides residues in honeybees that lives in colonies near to crops. It was optimized a QuEChERS method to extract pesticides from the honeybee samples, and the final extracts were analysed by Liquid Chromatography couple to tandem Mass Spectrometry (LC-MSMS) with a triple quadrupole detector.

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PO-48: Effects of Magnetic Nanoparticle Design Parameters on Magnetic Hyperthermia Processes

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Keywords: Magnetic nanoparticles, Magnetic hyperthermia

The ability of magnetic nanoparticles (MNPs) to generate heat upon exposure to external magnetic fields, known as magnetic hyperthermia, has been exploited in recent years as a cancer adjuvant treatment. This has allowed its clinical translation in patients with glioblastoma (Germany, 2011) and, more recently, in patients with pancreatic cancer (Spain, 2022). However, despite the continuous improvements in chemical synthesis processes, certain effects of MNPs once it is internalized in biological entities, such as aggregation or immobilization, and the reduced amount that can be inoculated into the organism, cannot be modulated. These experimental conditions affect the magnetic hyperthermia driving mechanisms, Néel and Brown relaxation, and limit its performance in biological applications. Therefore, a detailed knowledge of the set up parameters, as the possible interaction effects or the behaviour of MNPs in high viscosity environments, but more importantly the intrinsic properties of the MNPs, are key to maximize the response in magnetic hyperthermia. In this sense, during the last few years much effort has been devoted to improving Néel relaxation by optimizing the anisotropy constant [1-2].

In this work, the use of different design parameters in the synthesis of MNPs and its influence on magnetic hyperthermia processes are studied. To this end, different types of synthesis and the effects of the variation of the reagents used on the physicochemical properties and possible interaction effects are explored. Finally, the variation of the different parameters in the temperature increase obtained by the application of alternating magnetic fields using an AC magnetometer (AC hyster, Nanotech Solutions) and a commercial hyperthermia equipment (Magnetherm, Nanotherics) is correlated.

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PO-49: Antioxidant Capacity of Biopolymer Films Reinforced with Green Carbon Dots as Active Protection for Oil-Based Products

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Keywords: carbon nanomaterials, antioxidant activity, biofilm reinforcement, oil-based products conservation

The oxidation of oil-based products causes a considerable degradation in their quality and inherent properties. This process supposes a reduction of the nutritional value of edible oils[1] and a devaluation of the physicochemical properties of oils with industrial applications[2]. In that context, we test the antioxidant capacity of bio-polymer-based films (BPFs), made by methoxylated pectin (HMP) and sodium caseinate (CAS), and reinforced with green Carbon Dots (gCDs), obtained from natural sources like rosemary powder (RCDs) and apple pomace (APCDs), to prevent the oxidation of oil-based products. The incorporation of gCDs improves the antioxidant capacity of the raw biofilm, which increases up to 42% and 62% when it is enriched with 1% of RCDs and APCDs, respectively. The results obtained by determining the Peroxide Value (PV) of the oils, related to the formation of hydroperoxides in the samples, showed that the presence of gCDs-BPFs decreased the oxidation process of the oil in contrast to those without films, where it was observed a more noticeable increase in PV. Other studies revealed that the surface roughness of the films also changes depending on the type and concentration of gCDs used, obtaining a more homogeneous and less rough surface in RCDs-BPFs, even at the highest evaluated concentration (1% RCDs). In addition, stability studies based on intrinsic fluorescence signals of oil and gCDs demonstrate that gCDs are not released from the film due to their low dispersibility in the hydrophobic medium. In light of this, gCDs-BPFs developed could be promising materials to produce sustainable and biodegradable active packaging and prevent the deterioration of oil-based products.

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PO-50: Proteomic analysis of Mesenchymal Stem Cells Secretome from Human Uterine Cervix and its Therapeutic Potential

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Keywords: Proteomics, Liquid chromatography, Tandem mass spectrometry, Bioinformatics, Functional analysis.

Nowadays, research on Mesenchymal Stem Cells (MSCs) and their potential application in regenerative medicine have attracted significant interest. MSCs can be extracted from different tissues (i.e. bone marrow, umbilical cord blood or adipose tissue…) and recently, the Research Unit from Jove´s Hospital has isolated, identified and characterized a new type of MSCs from the uterine cervix (hUCESCs) which has antitumoral, anti-inflammatory and regenerative properties [1].

Moreover, hUCESCs secretes to the culture media a variety of biologically active substances while it's *in vitro* proliferation. This whole set of molecules is called "conditioned media" (CM) or "Secretome" and it can be inoculated to the patients instead of the MSCs [2]. Recent studies have shown promising results with both hUCESCs and the conditioned medium in which these cells was cultured (CM-hUCESCs).

For clinical translation of secretome-based treatment, characterization of its composition is needed to identify the contribution of different components/fractions to the therapeutic value of the Secretome. For this purpose, a whole proteome analysis of three CM-hUCESCs were carried out by nanoHPLC-ESI-MS/MS with a previous tryptic digestion. In the three samples analysed, 437 common proteins were detected and identified. Posterior functional analysis was made to categorize the proteins' function and their biological pathways. These results show a strong functional correlation between the found proteins which could explain the therapeutic potential of CM-hUCESCs. The identification of the secreted protein components with therapeutic effects is expected to be useful for future breast cancer therapy.

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PO-51: Engineered Nanorods and Nanowires of Different Metals for Cancer Therapies: Characterization by SP-ICP-MS

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Keywords: Nanowires, nanorods, SP-ICP-MS, drug delivery, photothermal therapy

Traditional therapeutics of cancer show limitations such as drug resistance or several adverse effects. To overcome these limitations and develop more efficient and less invasive methodologies, multifunctional nanosystems can be used instead, as they offer an enhancement of the treatment efficiency and a decrease in drug toxicity. They bring the choice to introduce specifically focused therapies on diseased cells and deliver the given treatment without damaging the healthy ones.

One of the most used nanosystems for this purpose are iron nanowires (Fe NWs). These magnetic nanowires bring many advantages over traditional NPs in terms of the application into therapeutics: they show a larger surface area and can be easily (bio)functionalized to enhance their biocompatibility, leading to a more selective intracellular drug delivery while side effects are lowered.

Another nanosystem with these biomedical applications are platinum nanorods (Pt NRs). They are used for the latest therapeutic strategy to treat cancer, photothermal therapy (PTT): a minimally invasive platform that induces selective ablation of cancer cells by heat generated in tumor tissue exposed to near-infrared (NIR) light. Pt nanorods are the best potential photothermal therapy agent as they exhibit strong light absorption and efficient light-to-heat conversion.

In this work, the characterization of these multifunctional nanosystems will be carried out in order to study their physical properties as an initial approach for further biological applications.

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PO-52: Effect of Synthesis Conditions of MIL-101(Cr)-SO_3H

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Keywords: MOFs, synthesis, MIL-101(Cr)-SO_3H

Metal–organic frameworks (MOFs) have great potential. However, it is known that small changes in their synthesis conditions can affect their final properties.

In this study, three different batches of MIL-101(Cr)-SO_3H were synthesised using a likewise protocol adapted from [1], albeit with subtle changes, to evaluate the effect of the synthesis conditions on the properties of the final MOFs. A mixture of $Cr(NO_3)_3{\cdot}9H_2O$ (2.0 g), H_2BDC-SO_3Na (2.7 g), deionised water (30 mL), and hydrofluoric acid (HF) (40 wt %) was heated at 190 °C for 24 h in a Teflon lined Parr 4744 reactor. The solid product was: (i) recovered by centrifugation or filtration; (ii) washed with deionised water, dimethylformamide (DMF) and acetone, or with water and methanol; and (iii) activated under vacuum up to 393 or 403 K. The specific conditions are summarised in the following table:

Batch #	ml HF (40 wt.%)	Purification solvents	Separation technique	Activation temperature (K)
1	0.30	Water, DMF and acetone	Centrifugation	403
2	0.36	Water, DMF and acetone	Vacuum filtration	393
3	0.38	Water and methanol	Vacuum filtration	393

The MOFs were characterised by powder X-ray diffraction (PXRD), infrared spectroscopy, adsorption of N_2 at 77 K, thermogravimetric and elemental analysis.

The PXRD spectra of **1**, **2** and **3** showed the expected peaks [1,2]. However, **1** showed a loss in crystallinity after activation at 403 K. Therefore **2** and **3** were activated at 393 K. The N_2 adsorption isotherm of **1** does not show the characteristic steps. Moreover, **1** presents a significantly lower pore volume than **2** and **3** (0.39 *versus* 0.74 and 0.88 cm^3/g, respectively). This might be related to the loss of crystallinity observed after activation at 403 K. The highest pore volume of **3** compared to **2** is mainly attributed to the substitution of DMF and acetone by methanol during the purification stage.

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PO-53: Evaluation of Matrices Effect on Organic Additives Performance in Solution Cathode Glow Discharge-Optical Emission Spectrometry

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Keywords: solution cathode glow discharge; plasma-liquid interaction; matrix effect; additives; seawater.

Solution cathode glow discharge (SCGD) is an atmospheric pressure operating source for optical emission spectrometry (OES) used in elemental analysis, consisting of a metallic anode and a flowing liquid cathode. SCGD-OES not only holds the comparable elemental sensitivity with that obtained with Inductively coupled plasma (ICP)-OES, but also presents advantages such as simple construction, low running costs and the possibility for in-situ analysis. Its improved performance when adding formic acid (HCOOH) is highly dependent on sodium chloride (NaCl) concentration. In the present work, other common cations and anions (K^+, Mg^{2+}, Ca^{2+}, $SO4^{2-}$, Br^-, NO_3^-, HCO_3^- and Br^-) were investigated to study their influence on the positive HCOOH effect on the elemental emission. The presence of alkaline metals led to variations on the HCOOH beneficial effect, while alkaline-earth metals and different anions did not. The disturbance of alkaline metals seems to come from analyte transfer efficiency from solution into the plasma, and not from a deterioration of the excitation conditions, marked by the small variations of elemental spatial patterns caused by HCOOH. Nevertheless, some volatile species forming elements (Hg, Ag, Pb or In) are not affected from the disturbance of alkaline metals in terms of HCOOH performance. In addition, experiments regarding the performance of acetic acid (AA), methanol (MeOH) and ethanol (EtOH) in various matrix solutions were carried out, suggesting that the additive influence on elemental emission relies on the functional group. The additive performance in artificial seawater resembles the case in the solution contain 59.8 mM NaCl due to the high proportion (67% of total salt) of NaCl in seawater.

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PO-54: Synthesis of New Phenethylamine-Azulene Conjugates via Regioselective Ring Opening of 2-Aryl-*N*-sulfonyl Aziridines

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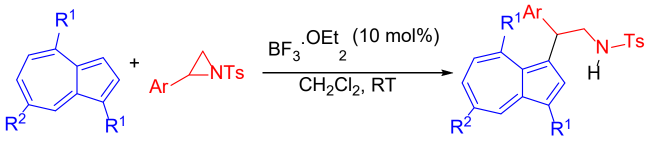
Keywords: Azulene, aziridines, phenethylamines, Lewis acid catalysis, ring-opening

Owing to the presence in the structure of several bioactive compounds, phenethylamines are considered valuable and highly sought-after frameworks in medicinal chemistry[1]. On the other hand, azulene derivatives have found many applications in different areas of science[2]. Despite their potential interest, the synthesis of phenethylamine-azulene conjugates remains challenging[3]. In this regard, we posited that these hybrids could be available through ring opening reaction of 2-aryl-*N*-sulfonyl aziridines. Herein we report the realization of this goal; specifically, we describe the Lewis acid-catalyzed reaction of azulene (**1a,** $R^1 = R^2 = H$) and 2-aryl-*N*-sulfonyl aziridines **2** providing new phenethylamine-azulene conjugates **3** in good yields (Scheme 1). This ring opening of the aziridine takes place with complete regioselectivity. A range of sterically and electronically differentiated aryl-substituted aziridines is compatible with this transformation. Guaiazulene (**1b,** R^1 = Me; R^2 = *i*Pr), a naturally occurring azulene derivative, is also a suitable substrate in this ring opening reaction. Further efforts aimed to expand the scope of this transformation are underway in our group.



1 **2** **3**

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