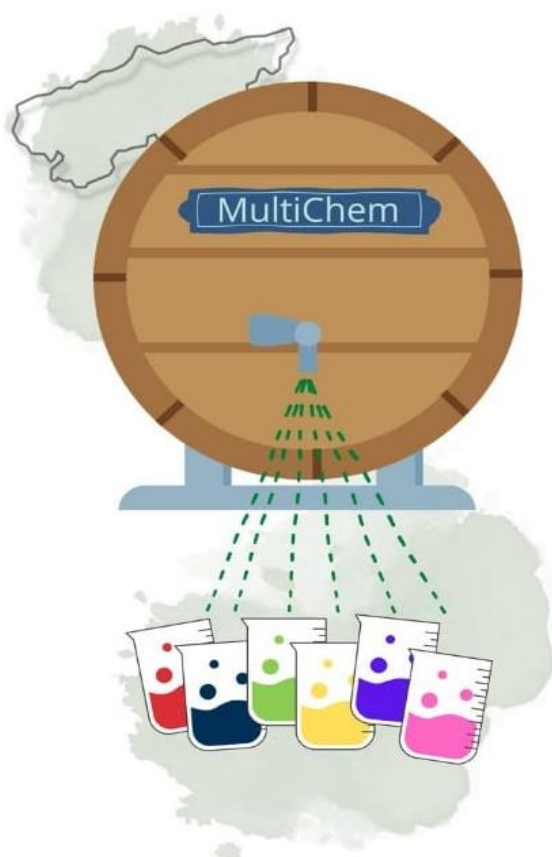


II PhD Multidisciplinary Chemical Congress



BOOK OF ABSTRACTS

March 14-15th, 2024
Escuela Politécnica de Ingeniería de Gijón (EPI)
University of Oviedo



WELCOME

We would like to present the second edition of the **PhD Multi-disciplinary Chemical Congress** aimed at PhD students in Chemistry or any related area, which will take place on March 14 and 15, 2024 at the Escuela Politécnica de Ingeniería de Gijón, Gijón (Principality of Asturias), University of Oviedo.

In this edition, as in the previous one, doctoral students are the key players of the congress, both in its organization and in the development of the event. A multidisciplinary space where we can actively participate disseminating our scientific production and promoting collaboration between the different branches of chemistry will be created.

This congress, promoted by the Territorial Section of Asturias 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 younger generations.



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Program



Thursday, March 14th

9:00 – 9:30	Opening Ceremony
9:30 – 11:20	Session 1 Chairperson: Mario Díaz Fernández (<i>University of Oviedo</i>)
9:30 – 10:30	Plenary Chemistry at the Crossroads: New Social Challenges through Science <i>Rosa Menéndez López (INCAR-CSIC)</i>
10:30 – 10:50	Keynote K-1 Lewis- and Brønsted-based Acid Deep Eutectic Solvents (ADESs). Efficient promoters of the alkyne hydration, Friedel-Crafts arylation and cascade reactions <i>Marina Ramos Martín (University of Oviedo)</i>
10:50 – 11:20	Flash Poster Session 1
	F-1: Development of a novel chemoenzymatic synthesis of tamsulosin <i>Enol de Prado Fernández (University of Salamanca)</i>
	F-2: ElectroELISA Probe: A new tool for on-site electrochemical ELISA readout of Epstein-Barr Virus serological tests <i>Ana Fernández Quesada (University of Oviedo)</i>
	F-3: Photo-biocatalytic deracemization of β -chlorohydrins <i>Sara Filgueira Fernández (University of Oviedo)</i>
	F-4: In situ bio-H ₂ production in biorefineries from syngas streams by steam reforming with integrated CO ₂ capture <i>Alejandra Vega Rodríguez (INCAR-CSIC)</i>
	F-5: DMPK optimization of a promising anti-alzheimer multitarget lead compound <i>Noemí Martínez-Conde (University of Barcelona)</i>
	F-6: Domain-averaged Local Spin Densities <i>Diogo José Lopes Rodrigues (University of Oviedo)</i>
	F-7: Photochemical Cross-Coupling of N-tosylhydrazones and boronic acids: a novel strategy towards geminal carboborylation reactions <i>Álvaro Valdés Maqueda (University of Oviedo)</i>
	F-8: Sustainable electrocatalysts for Oxygen Reduction in fuel cells <i>Elisa Martínez Díaz (INCAR-CSIC)</i>

F-9: Biogas Purification using a Pinecone Leaf-based Activated Carbon: Assessment of the Adsorption Capacity

Diego Cimadevilla Cabeza (INCAR-CSIC)

F-10: Photocatalytic oxidative cleavage of styrenes followed by carbonyl bioreduction towards stereoselective alcohol synthesis

Laura Rodríguez Fernández (University of Oviedo)

11:20 – 11:30 ArcelorMittal

11:30 – 12:00 Coffee break – Poster Session 1

12:00 – 13:50 Session 2

Chairperson: Inmaculada Ortiz (*University of Oviedo*)

12:00 – 12:20 Keynote K-2

Studying the bioaccumulation of metal nanoparticles in edible wild mushrooms

Andrés Suarez Priede (University of Oviedo)

12:20 – 12:35 Oral O-1

MgSO₄ as an effective, low temperature sulfur dopant for carbon materials enabling fast sodium storage

Sara Payá González (INCAR-CSIC)

12:35 – 12:50 Oral O-2

Chemoenzymatic concurrent cascade involving gold(I)-catalyzed Meyer-Schuster rearrangement of racemic propargylic alcohols and stereoselective bioreduction using ene-reductases

Lorena Escot Navarro (University of Oviedo)

12:50 – 13:05 Oral O-3

New electrochemical insights of nitrate reduction reaction on PtPd bulk alloy single-crystals

Pepe Jordá-Faus (IUE-University of Alicante)

13:05 – 13:20 Oral O-4

Stroke differential diagnosis on the go: fast and decentralized detection of novel biomarkers using electroanalytical devices

Pablo Rioboó Legaspi (University of Oviedo)

13:20 – 13:35 Oral O-5

Extracellular vesicles of adipose tissue modulate the growth of cancer cells

Belén García Soler (*University of Oviedo*)

13:35 – 13:50	Oral O-6 Continuous Gas-Phase Photocatalysis for CO ₂ reduction with g-C ₃ N ₄ : a sustainable approach <i>Saloa Vaquero Vílchez (Bilbao School of Engineering-UPV/EHU)</i>
13:50 – 15:30	Lunch
15:30 – 17:05	Session 3 Chairperson: Julen Munárriz Tabuenca (<i>University of Zaragoza</i>)
15:30 – 15:50	Keynote K-3 Beyond the Black Box: Interpretable Quantum Chemical Topology <i>Miguel Gallegos González (University of Oviedo)</i>
15:50 – 16:05	Oral O-7 Developing effective synthesis of a wide range of multimetallic aerogels by microwave-assisted sol-gel methodology <i>Judith González-Lavín (INCAR-CSIC)</i>
16:05 – 16:20	Oral O-8 Synthesis of graphene-anchored NHC-Iridium catalyst by two routes for Oxygen Evolution Reaction <i>María González Ingelmo (INCAR-CSIC)</i>
16:20 – 16:35	Oral O-9 Methyl groups behaviour as Lewis acids and bases <i>Noushin Keshtkar (University of Zaragoza)</i>
16:35 – 17:05	Flash Poster Session 2
	F-11: Addition of nanoparticles to lightweight concrete for CO ₂ capture <i>Diego Panizo Martín (University of Oviedo)</i>
	F-12: Novel multitarget inhibitors with amyloid antiaggregating activity to treat Alzheimer's disease <i>Anna Sampietro Pifarre (University of Barcelona)</i>
	F-13: Unveiling electron distributions in the real space <i>Daniel Barrena Espés (University of Oviedo)</i>
	F-14: New Ru(III) NAMI-type complexes with anticancer activity <i>Manel Estruch Blasco (University of Sevilla)</i>

F-15: Microwave synthesis of new co-polypyrrole-polyketone for anion exchange membranes

Francesco Lanero (University of Padova)

F-16: Novel *helico*BODIPYs as CPL-active small organic molecules

Pablo Izquierdo Cazorla (Complutense University of Madrid)

F-17: Use of life microorganisms, fibre and polyphenols as possible dietary targets for microbiota modulation at early life stages

Eva Gómez Pérez (University of Oviedo)

F-18: Metal-doped carbon aerogels as electrode materials for non-enzymatic glucose sensors

Mario Sánchez Suárez (INCAR-CSIC)

F-19: Determination of proteins in hypoxic Müller glia cells by single cell ICP-MS: the use of DNA intercalators for enhanced cell detection

Alicia Villa Vázquez (University of Oviedo)

F-20: 3-Nitro-2*H*-chromenes: useful synthons in photoredox Giese reaction

Patrícia Inês Carvalho Godinho (LAQV/REQUIMTE-University of Aveiro)

17:05 – 17:45 Coffee break – Poster Session 2

17:45 – 19:20 Session 4

Chairperson: Manuel Plaza Martínez (*University of Oviedo*)

17:45 – 18:05 Keynote K-4

Acid-free two-step fructose to FDCA conversion for sustainable plastic production

Ane Bueno Viso (Bilbao School of Engineering-UPV/EHU)

18:05 – 18:20 Oral O-10

Biodegradation of polyethylene microplastics by microorganisms

Bess Alicia Newrick (University of Oviedo)

18:20 – 18:35 Oral O-11

Multi-elemental mapping of metallic samples with various matrices using fs-LA-ICP-MS

Cristian Soto Gancedo (University of Oviedo)

18:35 – 18:50 Oral O-12

Thermodynamics of solids made simple: Quasiparticle Theory

Ernesto Blancas Jiménez (University of Oviedo)

18:50 – 19:05 **Oral O-13**

Design and development of magnetic NPs for biomedical applications

Raúl Gimeno Ferrero (University of Sevilla)

19:05 – 19:20 **Oral O-14**

Use of design of experiments for optimizing the performance of natural-based adhesives for seed coating in Agriculture

Sara Fuster Esteso (University of Alicante)

Friday, March 15th

9:00 – 10:35	Session 5 Chairperson: Joaquín García Álvarez (<i>University of Oviedo</i>)
9:00 – 9:20	Keynote K-5 The quest for molecular diversity: leaving no stones unturned <i>Pau Nadal (University of Barcelona)</i>
9:20 – 9:35	Oral O-15 Controlling Pd and OH species in UiO-66 Metal-Organic Framework for Guerbet Reaction: optimizing Alcohol Chain Growth <i>Pedro Jesús Cantarero Gómez (Bilbao School of Engineering-UPV/EHU)</i>
9:35 – 9:50	Oral O-16 Detection of genomic DNA for marine species identification based on the use of gold nanoparticles and signal amplification <i>Patricia Alcázar (University of Oviedo)</i>
9:50 – 10:05	Oral O-17 NADH-mediated primordial amino acids synthesis <i>Noemí Nogal Rodríguez (Autonomous University of Madrid)</i>
10:05 – 10:35	Flash Poster Session 3
	F-21: Hydrolysed sewage sludge as biosorbent for methylene blue removal <i>Luis Romero (University of Oviedo)</i>
	F-22: LA-ICP-MS for quantitative distribution of (Bio)markers in Breast Cancer <i>Sara Escudero Cernuda (University of Oviedo)</i>
	F-23: Modular synthesis of new BODIPY dyes with strong NIR emission properties <i>Álvar Serrano-Pindado (University of Oviedo)</i>
	F-24: Preparation of starch films added with lactobionic acid for antibacterial application <i>Saliha Oussaid (University of Oviedo)</i>
	F-25: Design and optimization of an immunoassay for GFAP determination as biomarker for differential diagnosis of stroke <i>Cristina Álvarez Álvarez (University of Oviedo)</i>
	F-26: Inhibition of influenza H1N1 virus fusion: a study on aniline- and phenol-based compounds <i>Celia Escriche (University of Barcelona)</i>

F-27: Effect of operational conditions on the entrapment of microplastics (MPs) in secondary sewage sludge

Claudio Casella (University of Oviedo)

F-28: Characterization of human milk exosomes: pasteurization effects

Claudia Gómez Martínez (University of Oviedo)

F-29: Synthesis and reactivity of 2-(aminomethyl)BODIPYs. Significance in BODIPY functionalization chemistry

Sergio Serrano Buitrago (Complutense University of Madrid)

10:35 – 11:15 Coffee break – Poster Session 3

11:15 – 13:30 Session 6

Chairperson: Vicente Gotor (*University of Oviedo*)

11:15 – 11:30 Oral O-18

From Green Gold to Black Gold: highly porous carbons from pistacchio shells by a controlled physical activation process

Ana Fernández-Lera González (INCAR-CSIC)

11:30 – 11:45 Oral O-19

Innovative sensor design for monitoring and mitigating the impact of bisphenol a on human health and ecosystems

Sandra Rodríguez Varillas (University of Oviedo)

11:45 – 12:00 Oral O-20

Bio-based starch nanoparticles with controlled size as antimicrobial agents

Diana Morán Tuya (University of Oviedo)

12:00 – 12:15 Oral O-21

CO₂ hydrogenation on Ru encapsulated on silicalite: a multiscale study

Manuel Antonio Cánovas Montes (University of Barcelona)

12:15 – 12:30 Oral O-22

Remodelling tumor microenvironment with small molecules: synthesis of new podophyllotoxin dual target hybrids with cytotoxic and immunogenic activity

Pablo López Fernández (University of Salamanca)

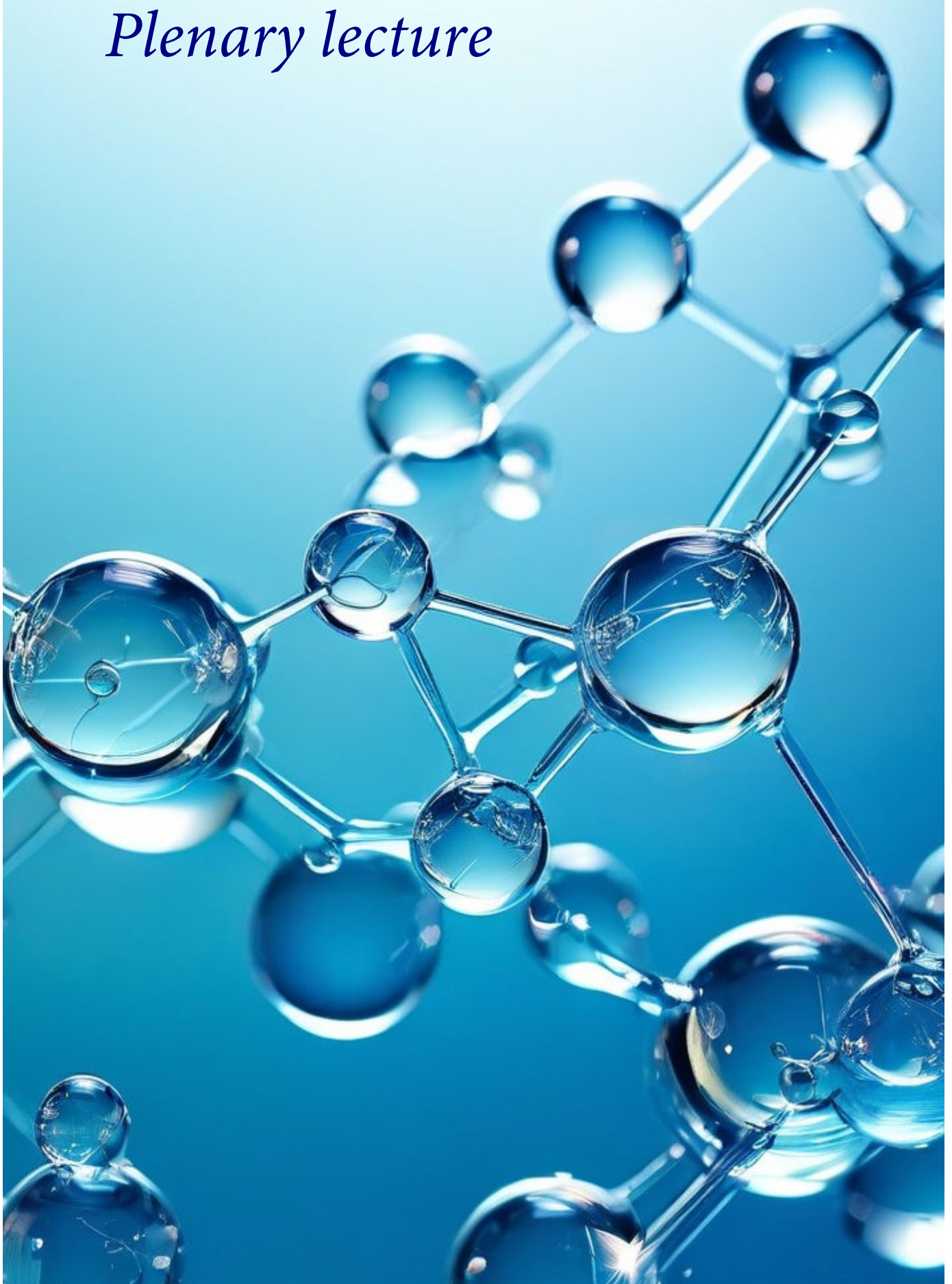
12:30 – 13:30 Plenary

Ángela Santianes

Country Leader of DuPont in Spain and Portugal

13:30 – 14:00 Closing Ceremony

Plenary lecture





Chemistry at the Crossroads: New Social Challenges through Science

Rosa Menéndez

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In the 21st century, the challenges facing science and technology are multifaceted and require interdisciplinary approaches for effective solutions. Chemistry, as a fundamental science, plays a crucial role in addressing these challenges due to its versatility and applicability across different fields.

Moreover, chemistry intersects with other scientific disciplines, such as biology, physics and materials science, contributing to their development, and leading to advancements and innovations. Collaborations between researchers from different fields foster creativity and facilitate breakthroughs that address complex problems. This is the case of the development of nanotechnology involving chemists, physicists, and engineers, leading to novel medical diagnostics and drug delivery systems, or the development of clean energy technologies, such as solar cells, fuel cells, and energy storage devices, which contribute to mitigate the global energy crisis and climate change.

This presentation intends to address these aspects from personal experience, providing illustrative examples.

Keynotes





Lewis- and Brønsted-based Acid Deep Eutectic Solvents (ADESs). Efficient promoters of the alkyne hydration, Friedel-Crafts arylation and cascade reactions

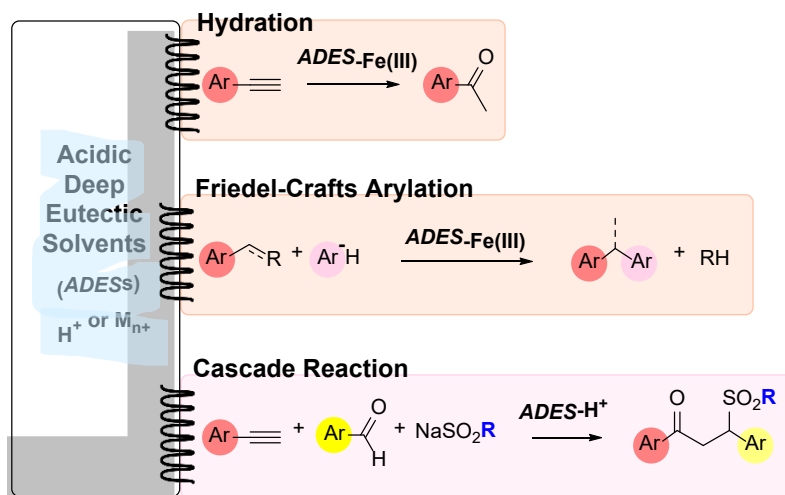
Marina Ramos-Martín¹, Joaquín García-Álvarez¹, Alejandro Presa Soto¹

¹ Laboratorio de Química Sintética Sostenible (QuimSinSos), Departamento de Química Orgánica e Inorgánica (IUQOEM), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Química, Universidad de Oviedo. C/Julián Clavería 8, 33006, Oviedo (Spain)

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Keywords: Acidic deep eutectic solvents, hydration, arylation, cascade reactions, sulfones.

Deep eutectic solvents have been established as one of more convenient sustainable reaction media in organic and inorganic synthesis. Among them, the so-called *Acidic Deep Eutectic Solvents (ADESs)* have been received increasing attention due to their dual role in as solvent and catalysts in a variety of synthetic procedures.[1] In this communications we show the versatility of these solvents in chemical synthesis by: a) the use of the Fe(III)-based *DES* (3FeCl₃·6H₂O/1Gly) to promote the hydration of alkynes[2] and Friedel-Crafts arylation for the formation of C-C bonds using a wide variety of reaction substrates and arenes; and b) the use of pTSA-based *DES* (2pTSA·H₂O/ChCl) to promote cascade reactions for the formation of γ -Keto Sulfones, a variety of compounds with biological and pharmacological activity.[3]



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

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- [3] *J. Chem. Pharm. Res.* **2019**, 2, pp. 253-255.



Studying the bioaccumulation of metal nanoparticles in edible wild mushrooms

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Keywords: Metallic nanoparticles, mushrooms, bioaccumulation, single particle-ICPMS

Metal nanoparticles (NPs) are a subject of growing interest in scientific research due to their unique properties and diverse applications. Their origin can be both natural (geogenic and biogenic) or synthetic. As these nanoparticles are increasingly incorporated into products and derivatives of human activity, their presence and accumulation in the environment is on the rise. Several studies have indicated that metal nanoparticles exhibit higher toxicity to organisms compared to similar concentrations of non-nanoparticulate metals [1].

While the absorption and accumulation of trace metals in soils by various organisms have been extensively studied, detailed research on the behaviour of metal nanoparticles in this context is still limited. Fungi, known for their ability to absorb and bioaccumulate metals, represent a particularly interesting group of organisms in this regard. Moreover, some studies have highlighted the ability of fungi, including the well-known mushrooms, to biogenically produce nanoparticles [2]. Given the importance of mushrooms in the human diet, it becomes essential to investigate the presence and bioaccumulation of metal nanoparticles in these organisms. This study employs four sets of samples from *Boletus edulis* and *Boletus aereus* from different locations, including samples from the growth soil, to attempt to study their ability to produce and/or absorb and accumulate metal nanoparticles present in the environment, as well as to characterize them.

Different analytical techniques are described to be optimal for this kind of studies. Among them, single particle analysis by inductively coupled plasma-mass spectrometry (SP-ICP-MS) has been already employed to characterize selenium nanoparticles in different mushroom species [2]. It was then applied in this work to address the presence and characteristics of metallic nanoparticles in the mentioned fungi samples. Additionally, high resolution transmission electron microscopy (HR-TEM) with energy-dispersive X-ray spectroscopy (EDX) was used as complementary technique to elucidate more data about the NP's size and composition.

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Beyond the Black Box: Interpretable Quantum Chemical Topology

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Keywords: QCT, Machine Learning, XCAI, SchNet4AIM

In the realm of machine-learned computational chemistry, a curious paradox has emerged: though molecular properties can be precisely foretold, understanding these predictions remains elusive. While Explainable Artificial Intelligence (XAI) tools offer insights into complex models, their efficacy is limited by the AI technique and reference data origin. Moreover, most XAI attempts rely on extrinsic tools which interpret the model's decision-making processes without directly addressing the underlying intricacies. Bridging this gap, we introduce SchNet4AIM, a SchNet-based [1] neural network architecture able to accurately predict local one-body (atomic) and two-body (interatomic) quantities. The outstanding performance of our approach is demonstrated through the accurate and fast estimation of various real-space quantities grounded in the framework of Quantum Chemical Topology (QCT) such as atomic charges or delocalization indices, among others. Besides accurate, the combination of SchNet4AIM with physically rigorous theories grants the models with a remarkable transferability and interpretability. In this way, our approach bypasses the bottleneck impeding the utilization of real-space chemical descriptors in intricate systems. Notably, the SchNet4AIM group delocalization indices serve as valuable indicators of supramolecular binding events, while allowing the on-the-fly identification of the most dominant pairwise components to the latter. Altogether, SchNet4AIM constitutes a fundamental example of Explainable Chemical Artificial Intelligence (XCAI) models.

Acknowledgments: The authors kindly acknowledge the Spanish MICIU, project PID2021-122763NB-I00, for financial support. Miguel Gallegos specifically acknowledges the Spanish MICIU for the predoctoral grant (No. FPU19/02903 and EST22/00100).

References:

[1] Schütt, K. T., Sauceda, H. E., Kindermans, P.-J., Tkatchenko, A. & Müller, K.-R. *J. Chem. Phys.* **2018**, 148, 241722.

Acid-free two-step fructose to FDCA conversion for sustainable plastic production

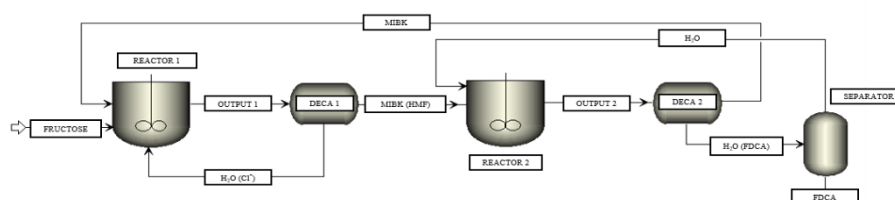
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Keywords: biomass, fructose, FDCA, sustainable technologies, PET.

This research explores the fructose conversion into 2,5-furandicarboxylic acid (FDCA), a critical precursor to polyethylene furanoate (PEF), providing a sustainable alternative to fossil-based polyethylene terephthalate (PET). The process entails an initial dehydration step, transforming fructose into 5-hydroxymethylfurfural (HMF), followed by an oxidation step to convert HMF into FDCA. While existing research has predominantly focused on these steps independently, the study introduces an innovative integrated system (**Scheme 1**) which has allowed the results obtained in the research to be patented [1].



Scheme 1. Integrated system for the production of FDCA.

In the initial phase, wherein the necessity of an acid catalyst is absent, the use of a biphasic system (H₂O/MIBK) with NaCl proves instrumental in promoting the transfer of HMF from the aqueous to the organic phase. This mechanism effectively prevents unwanted rehydration process leading to levulinic acid formation. Additionally, NaCl acts as a catalyst in the dehydration reaction, potentially inhibiting the activation of the C-C bond, a pivotal step in regulating the conversion of HMF to levulinic acid [2]. This system achieves a 100% fructose conversion, yielding up to 80% HMF (**Fig. 1.a**). In the second stage, a gold catalyst supported on hydrotalcite is synthesized for efficient HMF to FDCA conversion, benefiting from gold's oxidation properties and hydrotalcite necessary basicity. Due to the detrimental effect of chlorine ions on the catalyst, a pre-decantation step is suggested to recirculate chlorine ions with water, exclusively feeding the organic phase to the second reactor. It is noteworthy that in the absence of salt, FDCA yields exceeding 99% are attainable (**Fig. 1.b**).

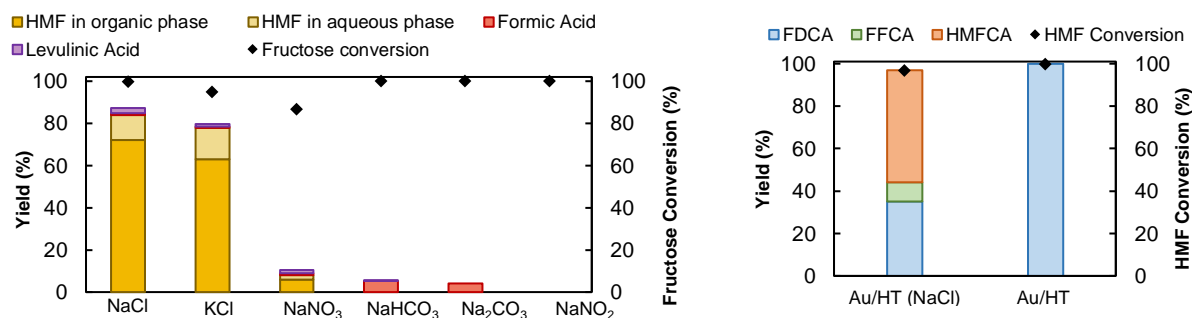


Fig 2. a) Salt effect in dehydration step; **b)** Au/HT catalyst effect on the oxidation step depending on the salt existence.

References:

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 [2] Mellmer, M.A.; Sanpitakseree, C., **2019**, 10.

The quest for molecular diversity: leaving no stones unturned

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Keywords: reaction charting, chemical space, reaction discovery, multicomponent reactions, molecular diversity.

Multicomponent reactions (MCRs) are potent tools in the quest for molecular diversity, as they deliver unconventional connectivity and allow for the rapid construction of chemical libraries with high appendage variety.^[1] Moreover, the discovery of new MCRs serves to explore uncharted regions of the chemical space through the generation of new molecular skeletons. Although this discovery is usually credited to a certain level of serendipity, in recent years several strategies have been developed to promote the rational design of MCRs, which have undeniably empowered the field.^[2] We believe that controlled tuning of an MCR – through a careful charting of the chemical reaction space – can help us navigate through its possible reaction pathways, to selectively reach different outcomes.^[3]

Our group focused on the combination of carbonyls, amines, and isocynoacetates, and described a new general multicomponent process to yield compounds **1**, close analogs of the green fluorescent protein chromophore. Adjusting the reaction conditions and inputs led to the selective formation of a range of related scaffolds. Ensuing chemistry upon these isolated adducts further expanded the chemical diversity generated from three simple off-the-shelf reagents (Figure 1). The generated compounds **2-8** comprise fused and spiro heterocycles and include kinase inhibitors and natural product analogues.^[4]

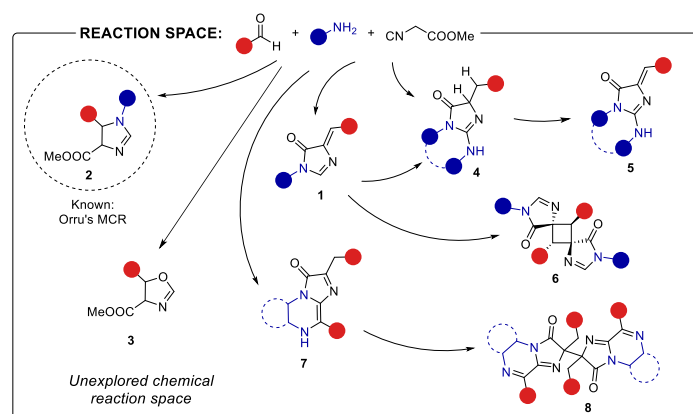


Figure 1. Charting the unexplored reaction space of an MCR combination.

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- [4] P. Nadal Rodríguez, O. Ghashghaei, A. M. Schoepf, S. Benson, M. Vendrell, R. Lavilla, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303889.

Oral communications





MgSO₄ as an Effective, Low Temperature Sulfur Dopant for Carbon Materials Enabling Fast Sodium Storage

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Keywords: S-doped carbon, magnesium sulfate, sodium storage, sodium-ion battery, sodium-ion capacitor

S-doping has been shown to be a powerful tool to boost the sodium storage performance of hard carbons. However, developing efficient, sustainable doping strategies is still a challenge. Herein we show the effectiveness of MgSO₄ as S-dopant compared to other traditionally used sulfates such as Na₂SO₄ and K₂SO₄. Thereby, even at a low carbonization/doping temperature of 600 °C, the glucose-based carbon material achieved a sulfur content as high as 26 wt%, compared to < 1 wt% obtained using Na₂SO₄ or K₂SO₄. This is translated into a Na storage capacity as high as 640 mAh g⁻¹ at 0.1 A g⁻¹ (compared to < 200 mAh g⁻¹ for Na₂SO₄-/K₂SO₄-derived carbons and the non-doped material) and still 122 mAh g⁻¹ at a high current density of 10 A g⁻¹. Furthermore, it is shown that this S-doping tool not only promotes the redox activity at high potentials, but also the low potential capacity (usually below 1.5 V vs. Na⁺/Na) exploitable in Na-based technologies. This feature coupled to the enhanced reversibility of Na storage (ICE of ca. 80 %) induced by the S-doping, supports the suitability of this material as negative carbon electrode in Na-based batteries and hybrid capacitors. Further engineering through nanostructuring improves the kinetics at high rates in the usable low potential region, which proves the beneficial effect of the templating technique coupled to doping. The universality of the synthesis strategy is shown by successfully applying it to biomass products and wastes.

Acknowledgments: This research work was supported by project IDI/2018/000148 (FICYT/FEDER) and PID2021-123648OB-I00 (MCIN/AEI /10.13039/501100011033/ and ERDF A way of making Europe). S. Payá also thanks the Principality of Asturias for her Yo Investigo contract.

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Chemoenzymatic concurrent cascade involving gold(I)-catalyzed Meyer-Schuster rearrangement of racemic propargylic alcohols and stereoselective bioreduction using ene-reductases

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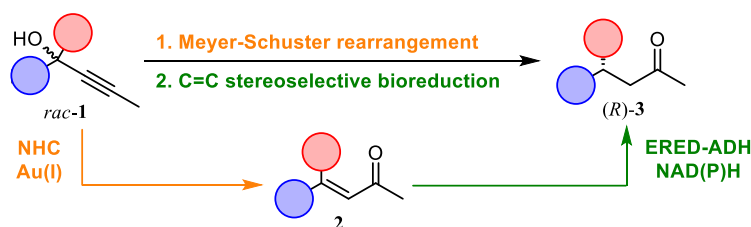
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Keywords: Asymmetric synthesis, Chemoenzymatic cascades, Ene-reductases, Gold catalysis, Meyer-Schuster rearrangement.

The integration of biocatalysis and organometallic chemistry presents fascinating opportunities to perform multi-stage transformations in a straightforward manner.[1] Importantly, gold(I) *N*-heterocyclic carbenes (NHC) and enzymes, such as alcohol dehydrogenases (ADHs) and amine transaminases, have been found to be suitable partners to obtain chiral alcohols[2] and amines,[3] respectively, from achiral substrates. Herein, an ene-reductase (ERED) and a NHC gold(I) catalyst, namely [1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene]-[bis(trifluoromethanesulfonyl)imide]gold(I) (IPrAuNTf₂), have been successfully combined for the first time. Thus, starting from racemic propargyl alcohols **1**, a Meyer-Schuster rearrangement produced the corresponding α,β -unsaturated ketone intermediates **2**, which served as ideal substrates for the *Zymomonas mobilis* reductase (NCR-ERED) towards the formation of the saturated chiral β,β -disubstituted ketones (*R*)-**3**.



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New Electrochemical Insights of Nitrate Reduction Reaction on PtPd Bulk Alloy Single-Crystals

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Keywords: Electrochemistry, Nitrate Reduction, Platinum, Palladium, Single-Crystals.

Nitrate reduction reaction (NO₃RR) is an important reaction in the treatment of wastewater and groundwater [1]. Traditionally, priority has been given to the reduction of nitrate (a polluting compound) to nitrogen gas [2] (harmless and not hazardous to the environment). Recently, interest is growing in obtaining other products like ammonia or hydroxylamine [3], which are essential reagents in the synthesis of several nitrogenated products, such as fertilisers, fuels or polymers.

Pt is a good catalyst for many electrocatalytic reactions of interest. However, it has low catalytic activity for the NO₃RR. Nevertheless, when a second metal is deposited, such as Pd, on a Pt(100) substrate (Pd-Pt(100)), the activity is considerably increased [4]. This has motivated us to go one step further and carry out fundamental studies using PtPd bulk alloy single-crystal electrodes (Pt_{100-x}Pd_x(100)), where both Pt and Pd metals are present in the first layer. Using these electrodes, further insights about the NO₃RR in terms of surface structure and composition can be obtained.

Pt_{100-x}Pd_x(100) electrodes were manufactured [5] and characterised electrochemically, recording their voltametric profile. Results for NO₃RR show a considerable increase in catalytic activity when Pd is present on the electrode surface in both acid and alkaline media. Comparing both media, in alkaline media, there is less overpotential, and apart from the NO₃RR current, an oxidation current is detected as well. To complement NO₃RR, NO reduction (NORR) has been studied to complement the NO₃RR study because it is a well-known reaction intermediate. Also, NO₃RR has been studied at different temperatures to obtain the activation energy.

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Stroke differential diagnosis on the go: fast and decentralized detection of novel biomarkers using electroanalytical devices.

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Keywords: acute stroke, GFAP, nasal exudate, bioelectroanalysis, immunoassays

Stroke constitutes a substantial global health issue, impacting approximately 15 million individuals per year, worldwide. Out of these, 33% of the cases end in death and an additional 33% are rendered permanently disabled. Stroke can be classified into ischaemic stroke (IS) and intracerebral haemorrhage (ICH). Each type requires a specific treatment and management. Thus, a quick and efficient differential diagnosis is critical to improve the patient's overall outcome. Current diagnostic procedures rely on neuroimaging, and, although several proteins in blood serum have been identified as promising biomarkers to differentiate between IS and ICH, sample extraction and processing is still time-consuming.

In this context, the concentration of glial fibrillary acidic protein (GFAP) in serum blood has been thoroughly studied as a differential stroke blood biomarker with diagnostic potential. Meanwhile, the discovery of cerebral glymphatic system has opened a new source of potential biomarkers in nasal exudate, with the added value of being a minimally invasive sample that collects information directly from the central nervous system. In this work, with the aim of moving from blood towards nasal exudate, we have studied the presence and concentration of GFAP in nasal exudate (nGFAP) as potential biomarker that could improve and speed up acute stroke diagnosis, being able to provide a result in minutes and in virtually any place.

For this purpose, sample collection has been optimized by comparing diverse collection devices and its protein recoveries using different processing protocols. Moreover, nGFAP levels have been studied in samples from IS and ICH patients, finding increased levels in ICH patients, correlated with an increase in serum GFAP [1]. Finally, in order to provide a decentralized diagnosis, an electrochemical two-step immunoassay-based device is being developed, with promising results of GFAP determination in less than 15 minutes.

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Extracellular vesicles of adipose tissue modulate the growth of cancer cells

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Keywords: Extracellular vesicles, adipose tissue, tumor microenvironment, cell communication.

Introduction: Adipose tissue plays a major role in metabolic and energy homeostasis, mainly through its endocrine activity. There are two main types of adipose tissue with different functions. White adipose tissue (WAT) plays a role as energetic storage while brown adipose tissue (BAT) is mainly thermogenic. While WAT is observed within tumours, and it is frequently associated to poor prognosis [1]. BAT has been linked to an improvement of metabolic homeostasis, but its role is poorly understood in cancer [2]. Recently, our group has found that BAT is enriched in the microenvironment of prostate cancer after androgen deprivation, a common treatment in clinics [3]. With this in mind, the purpose of this research was to find out the way of communication between white or brown adipose cells and tumour cells.

Materials and methods: Cell culture assays were performed with pre-adipocytes 3T3-L1 and hormone sensitive and resistant prostate cancer cell lines. 3T3-L1 cells were differentiated into an adipocyte-like phenotype and treated with the antiandrogen drug bicalutamide (CDX) triggering the differentiation into brown-like adipocytes. After confirmation of browning by UCP1 expression levels, cell communication was studied by co-culture systems. 3T3-L1 adipocytes extracellular vesicles (EVs) were isolated by ultracentrifugation and assayed as potential mediators. Also, murine fat pads were extracted and cultivated in control or browning conditions. These explants were afterwards implanted in adult mice and subsequently TRAMP C1 cells were injected. Tumours were measured periodically and extracted for morphological analysis.

Results: We found that after CDX treatment, 3T3-L1 cells overexpress the BAT marker UCP 1. Also, that EVs isolated from 3T3-L1 cells increased the growth of cancer cells, while EVs obtained from brown-like 3T3-L1 adipocytes prevented these increments. Moreover, fat pads differentiated to brown-like tissues reduced the growth of tumours implanted in adult mice.

Conclusions: Protective effects of brown-like adipocytes observed both in vivo and in vitro can be attributed to the content of EVs. EVs of brown adipocytes are load with different metabolites than white adipocytes, and this cargo causes a different response in tumour cells and deserve to be investigated.

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Continuous Gas-Phase Photocatalysis for CO₂ Reduction with g-C₃N₄: A Sustainable Approach

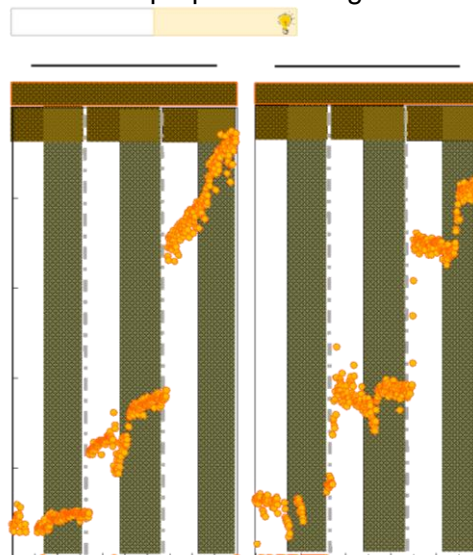
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Keywords: Photocatalysis, Carbon nitride, CO₂ reduction, Continuous gas phase

Photocatalysis represents an outstanding example of a sustainable process that has experienced significant advances in environmentally related applications through the use of semiconductor-based photocatalysts. Carbonitride (g-C₃N₄), a visible light sensitive material, stands out by differentiating itself from other semiconductors due to its suitable band gap for CO₂ reduction. In contrast, g-C₃N₄ can be easily prepared by thermal polycondensation of an inexpensive, nitrogen-rich precursor such as dicyanamide, melamine or urea¹. Gas-phase photocatalytic reactions represent a less explored, although promising, line, as they allow for higher product separation and purity². This study focuses on the application of a continuous photocatalytic reactor for heterogeneous gas/solid CO₂ reduction. The pilot plant consists of a double light-emitting cell, where a Xe lamp is used as a light source and which allows operation under pressure and temperature, thus allowing the study of the reaction kinetics. The reactor enables controlled deactivation through poisoning, allowing for the assessment of the active center's role in catalysis. In the present work, g-C₃N₄ has been prepared through thermal polycondensation of melamine. To enhance material photocatalytic properties and minimize recombination of photogenerated charges, a Pt co-catalyst has been incorporated at levels below 2%. In addition, thermal pretreatments using H₂ at different temperatures have been applied with the aim of conferring greater stability to the structure. In order to analyze the impact of doping with different metallic percentages and pretreatment, the optical and structural characterization of the material has been carried out. This approach seeks to establish correlations between these results and the catalyst activity. From the catalytic data obtained, an optimum amount of metal has been determined, the stability over time of the catalyst has been evaluated (Figure 1), the operating conditions have been optimized and the effect of light on the material has been studied.



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Developing effective synthesis of a wide range of multimetallic aerogels by microwave-assisted sol-gel methodology

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Keywords: sol-gel synthesis, microwave, transition metals, multimetallic aerogels.

Transition metal aerogels (TMA) have garnered significant attention in recent years due to their unique properties [1]. Among these types of materials, multimetallic aerogels (MMA) are postulated as the most interesting TMA as they can combine the features of different metals, giving rise to enhanced catalytic, electronic, and optical properties, rendering them promising candidates for their application in sensing, catalysis, and energy storage. Recently, a few studies have been published on the synthesis of MMA, but there is still a lack of in-depth understanding of its preparation, besides employing complex processes and toxic precursors. Furthermore, several hours of reaction are required, resulting in heterogeneous structures limiting their effectiveness and applicability [2]. This work proposes the use of microwave-assisted sol-gel synthesis for the production of MMA, which expedites the gelation process and facilitates the homogenous interaction between different non-toxic metal precursors, resulting in the formation of well-defined aerogel structures with controlled morphology.

MMA have been synthesized using different combinations of metallic precursors (Fe, Ni, Mn, and Co) in a microwave oven at 68°C for 1 h. After the synthesis, the MMA have been reduced in an H₂ atmosphere to a temperature determined by TPR, taking into account the maximum heating limit of the equipment and their morphology and porous properties have been characterized by SEM and N₂ adsorption/desorption isotherms, respectively. The nanostructure of MMA varies with the synthesis conditions, demonstrating the need to control the morphology at each stage of the process. In addition, the resulting materials exhibit a wide range of porous properties.

In conclusion, microwave-assisted sol-gel synthesis offers a viable route for the fabrication of multimetallic aerogels with a wide range of physicochemical properties. This research contributes to the expanding knowledge based on advanced aerogel materials and sets the stage for their broader utilization in cutting-edge technologies.

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Synthesis of graphene-anchored NHC-Iridium catalyst by two routes for Oxygen Evolution Reaction

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Keywords: graphene chemical functionalization, electrografting, water splitting

Water splitting is a crucial electrochemical reaction to produce sustainable hydrogen directly from water. The anodic reaction of this process, the oxygen evolution reaction (OER), is the bottleneck and requires the use of catalysts as iridium and ruthenium complexes. [1] For large-scale use of these catalysts, their efficiency and robustness can be enhanced through immobilization via covalent attachment to a support. Carbon-based materials, like reduced graphene oxides (rGO), acting as support offers additional advantages such as enhanced conductivity. Current efforts aim to efficiently immobilize catalysts on graphene surfaces while maintaining or even increasing the catalytic efficiency of the resulting hybrid material. In this work, we study and compare two different synthetic routes of in-situ covalent functionalization of rGOs with Ir complexes stabilized by a nitrogen ligand. The two preparation routes make use of the aryl diazonium salt chemistry [2] and consist of the following: (a) direct graphene electrografting of the previously synthesized imidazol-ylidene-Ir complex and (b) a two-step sequence comprising initial electrografting of the imidazolium ligand and subsequent chemical anchoring of the iridium precursors. The hybrid materials obtained and all intermediates were characterized using different techniques (XPS, EXAFS, ICP-MS) to confirm the expected structures. Their electrochemical performance in OER demonstrated the efficient catalytic activity of the supported imidazol-ylidene Ir/graphene hybrid materials prepared. A substantial increase of the current density was detected in the rGO films used as working electrodes after electrografting of the iridium complexes (route a) or after the linkage of the iridium precursor (route b), but only route b promotes adequate stability for a long-term electrode utilization.

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Methyl groups behaviour as Lewis acids and bases

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Keywords: Non-covalent interactions, DFT calculations, σ -hole interaction, methyl-methyl interactions

Methyl groups bonded to electronegative atoms such as N or O are well known to participate in tetrel bonding as Lewis acids[1]. On the other hand, it has recently been reported that methyl groups attached to electropositive atoms such as B or Al can act as Lewis bases[2]. In this work, we analyse the combination of these two behaviours to produce attractive methyl-methyl interactions.

A set of twelve E-CH₃···H₃C-Y (Y = -CH₃, -N(CH₃)₂, -OCH₃, -Br; E = (CH₃)₃-Si-, (CH₃)₃-Sn- and (CH₃)₂-Al) model systems was considered for a comprehensive computational investigation to unveil the nature and strength of these interactions. The results show that the calculated interaction energies are small, ranging from -0.5 to -1.2 kcal·mol⁻¹, being strongest for E = Al. NBO analysis revealed a significant charge transfer from bonding to antibonding carbon-based orbitals ($\sigma_{E-C} \rightarrow \sigma^*_{C-Y}$; see Figure 1), and the analysis of the topology of the electron density has shown that the interaction is localized between the two carbon atoms without contribution from C···H or H···H interactions, in good agreement with the negative penetration indices[3] obtained for these pairs of atoms in the model systems. Based on these results, the dimethyl interaction is characterized as weak but attractive, with a non-negligible contribution from orbital charge transfer and polarization[4].

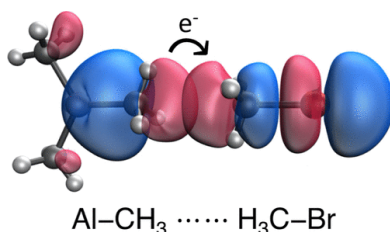


Figure 1. Donor and acceptor natural bond orbitals are involved in the $\sigma_{Al-C} \rightarrow \sigma^*_{C-Br}$ charge transfer process.

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Biodegradation of polyethylene microplastics by microorganisms

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Keywords: Microplastics, plastic pollution, biodegradation and bacterial degradation

In recent years, the exponential increase in the production of plastic materials has led to the generation of a large amount of waste, which currently represents an important environmental challenge [1]. One of the biggest issues caused by this type of pollution is the release of plastic particles into our ecosystem, known as microplastics (MPs). These small contaminants (<5 mm) are highly resistant to degradation, and have been detected in even the most remote habitats [2]. Their accumulation in terrestrial, aquatic, and atmospheric environments suppose a major threat to both humans and animals. Therefore, there exists an urgent need to control this microplastic pollution, through various technologies, such as biotechnological approaches including biodegradation by microorganisms.

This work evaluates the efficiency of the microorganisms *Comamonas testosteroni* and *Bacillus firmus* to carry out the biodegradation of high-density polyethylene (HDPE) microplastics at a concentration of 500 mg/L and a size range of 100-250 μm during an eight- and thirty-day long trial, respectively. It was found that the bacteria were able to utilise the HDPE microplastics for growth through the reduction of the initial polymer mass. The biodegradation experiments led to a weight loss of 12.30% after 8 days of incubation by *C. testosteroni*, and 15.5% after 30 days by *B. firmus*. Further evidence for the biodegradation was obtained using a scanning electron microscopy (SEM) analysis, which revealed the colonization and formation of a biofilm on the microplastics surfaces as well as possible signs of structural and morphological changes. Changes in the chemical and structural properties were also analysed through SEM-EDS and Fourier transform infrared spectroscopy (FTIR). The results show that *C. testosteroni* and *B. firmus* may contribute to the degradation of HDPE MPs and have further applications to avoid the multiple threats caused by microplastics accumulation.

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Multi-elemental mapping of metallic samples with various matrices using fs-LA-ICP-MS

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

The development in the metallurgical industry yearns for methods to precisely determine elements and their distribution in various metallic samples, such as coatings or welding points. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a well established technique for elemental mapping of solid samples. Moreover, using a femtosecond laser is highly beneficial in the analysis of metal samples due to its lower thermal and matrix effects [1]. Using a Time of Flight (ToF) with the fs-LA-ICP, allows to do a fast and precise mapping of every isotope in a range of 23-238 m/z. In this study we analysed the composition and elemental distribution, minimizing pretreatment, in a metallic sample composed of two very different matrices. The target sample has a steel matrix with a Hastelloy coating (Cr, Mo, Ni, W), which has been immersed in a corrosive bath. We aim to observe the possible inclusions and/or elemental migrations that could have happened during the fabrication process or the corrosive bath. Two maps were done, one unattenuated to observe trace elements, and one with a 35-factor of attenuation of the signal, to observe major elements. Data was treated to obtain a unique quantitative map of each element combining the data obtained from the two attenuations and using two different reference materials for a matrix-matched quantification.

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Thermodynamics of Solids Made Simple: Quasiparticle Theory

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Keywords: Anharmonicity, thermodynamic properties, compressive sensing, quasiparticle theory

The ability to predict thermodynamic properties of solids using reliable and efficient methods is fundamental in many fields, e.g., in the discovery of novel materials (superconductors, thermoelectrics, semiconductors for solar cells, etc.) or for systems under extreme pressure and temperature (geophysics and geochemistry). The quasi-harmonic approximation (QHA), based on the calculation of the volume-dependent harmonic frequencies ($\omega(V)$), is widely used because it provides a balance between reliability and computational cost, with excellent results for simple crystals. However, due to the underlying assumptions in QHA, this approximation breaks down for some systems at high temperature, as well as in the description of second-order phase transitions or in highly anharmonic crystals. Overcoming the limitations of QHA is not simple. Volume and temperature or effective frequencies ($\omega(V, T)$) cannot be used directly in the harmonic expressions for the thermodynamic properties and require the use of quasiparticle (QP) theory[1]. In this study we develop a new methodology based on QP theory and the calculation of effective frequencies in combination with compressive sensing. The first step of our methodology is the calculation of the anharmonic entropies with $\omega(V, T)$, which are then fit with a thermodynamically consistent model based on Debye's theory to obtain all thermodynamic properties of the solid under study, including the Helmholtz free energy and the constant-volume thermal conductivity. We showcase the new methodology with two examples for which QHA fails at relatively low temperatures, MgO and CaO, and demonstrate that it prevents the QHA blow-out at high temperature, yielding thermodynamic properties in much better agreement with experiment.

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Use of design of experiments for optimizing the performance of natural-based adhesives for seed coating in Agriculture

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Keywords: Design of experiments, optimization, gum Arabic, seed coating.

Seed coating consists in covering a seed with an adhesive for producing an external coating intended to alleviating biotic and abiotic stresses, thereby improving crop growth and yield. The coating of the seed surface makes possible adhering different products (biostimulants, biofertilizers), increasing their efficiency due to their better distribution. One common biostimulant is a mycorrhizal fungus embedded in a clay powder, this was selected in this study.

Different natural and synthetic adhesives have been proposed for seed coating, the gum Arabic-based adhesives have a potential for seed coating. Considering that the performance of the gum Arabic adhesives depends on their formulation, in this study, the design of experiments has been applied by using a full 2^k factorial design to optimize the amounts of each component for minimizing the dust emission (response variable) – the removal of adhered powder on the seed surface - in corn seeds coated with clay powder.

The selected factors were different amounts of gum Arabic - 10-20% by weight -, glycerol plasticizer - 1-10 phr (with respect to the gum Arabic content) and lactic acid natural biocide - 1-5 phr (with respect to the gum Arabic content). All adhesives were prepared in an aqueous solution of saponin surfactant.

The application of the design of experiments showed that the amounts of all components have significant effects on the dust emission, mainly the amount of gum (Figure 1), the dust emission of seeds coated with clay powder and gum Arabic-based adhesives is reduced (Figure 2).

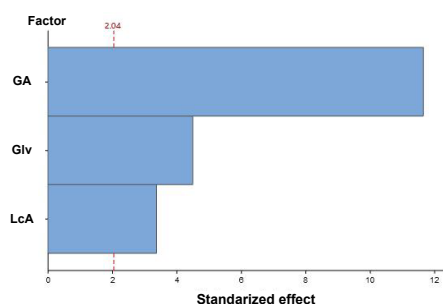


Figure 1. Standardized effect of different factors in dust emission. All factors pass the significance bar (2.04).

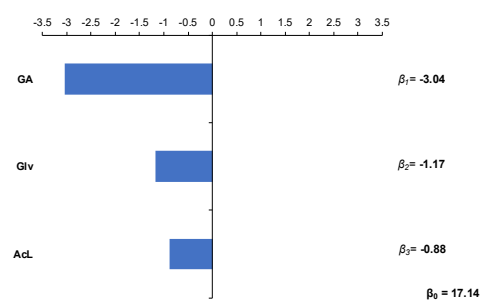


Figure 2. Effect of different factors in the dust emission. Negative values mean lower dust emissions.

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Controlling Pd and OH species in UiO-66 Metal-Organic Framework for Guerbet Reaction: optimizing Alcohol Chain Growth

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Keywords: Metal-Organic Frameworks, Palladium Nanoparticles, Alcohol Chain Growth, Guerbet Reaction, Characterization Techniques.

Metal-Organic Frameworks (MOFs) have emerged as novel catalysts to control the growth of alcohols. Diverse characterization techniques were necessary when UiO-66, a well-rounded MOF, was deeply investigated. X-ray diffraction (XRD) verified the crystalline nature of the material after treatments. Thermogravimetric analysis (TGA) facilitated the determination of average linker defects per formula. Additionally, Fourier-transform infrared spectroscopy (FTIR) monitored the material's evolution during post-pre-treatments, offering insights into the transformation of OH⁻ groups and MOF's chemistry in the metal cluster (Fig. 2a).

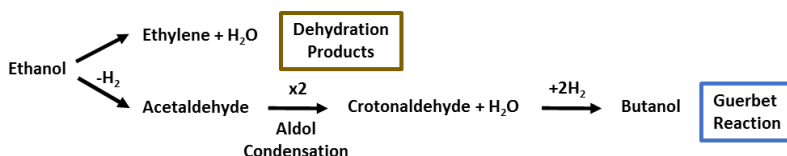


Figure 1. Ethanol reaction pathways in Pd-UiO-66: dehydration and Guerbet.

The initial segment focused on UiO-66's intrinsic acidity, performing acetaldehyde conversion (aldol condensation) without Pd species. Remarkable crotonaldehyde selectivities (95%) were achieved through systematic fine-tuning of MOF defects, acetaldehyde partial pressure, and temperature. Subsequent, control over the doping with Pd nanoparticles (NPs) and an optimal ratio with hydroxyls groups within MOFs could efficiently catalyze the three sequential steps in the Guerbet reaction: alcohol oxidation, aldol condensation and alcohol hydrogenation from ethanol¹. Finally, 1-butanol was produced, surpassing previously reported selectivities for UiO-66² (Fig. 2b). Posterior optimization revealed Pd-NPs and OH⁻ groups as pivotal in the ethanol to 1-butanol pathway, shifting pathways from dehydration towards the Guerbet reaction.

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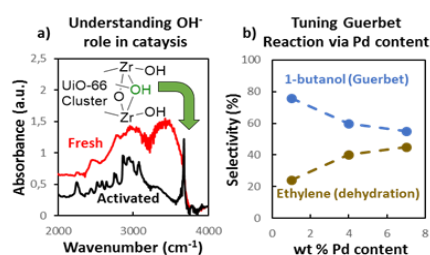


Figure 2. a) FTIR spectra of fresh and activated UiO-66. b) 1-butanol selectivity as function of Pd.



Detection of genomic DNA for marine species identification based on the use of gold nanoparticles and signal amplification

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Keywords: Nanoparticles, MNAzyme, signal amplification, fisheries, fraud

Artisanal fisheries are seriously threatened by socio-economic factors as well as by events related to climate change and overexploitation of fish stocks. Recent global analyses reveal that an average of 30% of seafood products worldwide are misdescribed or mislabelled. One of the reasons behind this is that not all fish catches are properly recorded, due to inaccurate species identification in fisheries landings [1]. Knowing the different biological units of commercial species is crucial for their sustainability and stock management. In recent years, nanotechnology and DNA-based techniques have been combined to achieve targeted and rapid detection of genetic sequences of interest [2].

The present work shows a methodology that takes advantage of the optoelectronic features of Gold Nanoparticles (GNPs) for colorimetric detection, based on changes of the surface-plasmon resonance absorption peak of dispersed and aggregated nanoparticles, that produce a colour change. In order to increase the sensitivity of the assay, an isothermal nucleic acid amplification technique called Multicomponent Nucleic Acid Enzymes (MNAzymes) is used [3]. With the use of MNAzymes coupled to GNPs, the aim is to identify the presence of certain marine species of commercial interest in real samples (tissues or environmental samples). Therefore, the first step is to carry out the assay with specific DNA from the species *Octopus vulgaris* and *Silurus glanis*, which are currently of special commercial or environmental interest. The aim is to design several types of MNAzymes that allow the detection of these species with the highest possible sensitivity, and to couple this technique to a rapid, simple microfluidic system that allows its use for visual detection *in-situ*.

Acknowledgments: Support for this work was provided by Project Eye-Fish-Track (MCINN-22-PDC 2022-133730-100).

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NADH-mediated primordial amino acids synthesis

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Keywords: NADH, non-enzymatic, biochemistry, amino acids, NMR

Nicotinamide adenine dinucleotide, NAD⁺ (and its reduced counterpart, NADH), is an important cofactor involved in multitude of redox reactions within the biochemistry of all living cells. These electron transfer reactions where coenzyme NAD⁺/NADH is involved are, in most of the cases, catalyzed by enzymes.

In the context of the origins of life, it is interesting to investigate non-enzymatic routes in which this coenzyme, can participate in redox reactions. Moreover, it is also desirable to gain deeper knowledge about the action mechanisms of these nicotinamide-based systems and their degradation pathways in prebiotic environments. In this framework, some prebiotic reactions in which NAD⁺ acts as oxidant have been reported.¹

Therefore, the study of NAD⁺/NADH and nicotinamide-based prebiotic analogues was envisaged by our group, given our experience in the field of prebiotic systems chemistry.^{2, 3} We chose the formation of amino acids through reductive amination as the model reaction to explore the non-enzymatic redox properties of nicotinamide systems, in light of the importance of investigating possible primitive sources of these biomolecules.⁴

Thus, we present a systematic study of the reductive amination in which ammonia, as nitrogen source, is incorporated into simple α -ketoacids a process mediated by NADH. This process could be considered as a primordial synthetic route to α -amino acids. Particular attention has been given to proposing a mechanistic hypothesis supported by DFT calculations and spectroscopic data.

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From green gold to black gold: highly porous carbons from pistachio shells by a controlled physical activation process

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Keywords: porosity, carbon, biomass, hydrothermal carbonization, and CO₂ activation.

Porous carbons are in high demand in a significant number of applications that are of great relevance for the transition to a more sustainable energy system, such as electrochemical energy storage and conversion devices (batteries, electrochemical supercapacitors, hybrid capacitors and as electrocatalysts in fuel-cells), or gas storage (hydrogen and methane storage). In many of these applications, it is important to control the porous structure of the material to achieve a high micropore development that maximizes the storage capacity of ions (supercapacitors) or gases. Chemical activation processes are usually used because they allow the greatest pore developments ($> 2000 \text{ m}^2 \text{ g}^{-1}$) and narrower pore size distributions, but in many cases the high toxicity and corrosivity of the activating agents speaks against their use. This work shows the possibility to obtain materials with similar characteristics, but via a more environmentally-sound process, i.e. through a physical activation process by using CO₂ as oxidizing agent and by carefully selecting the appropriate pre-treatment (acid pre-treatment, hydrothermal carbonization) of the biomass (pistachio shells). In this way, highly porous carbons with BET surface areas up to ca. $3300 \text{ m}^2 \text{ g}^{-1}$, pore volumes up to $1.6 \text{ cm}^3 \text{ g}^{-1}$, and pore size distributions centered in the micro- to small mesopore region ($< 3 \text{ nm}$) have been synthesized. As a result, these materials show high surface area density values, $> 2000 \text{ m}^2 \text{ cm}^{-3}$, which suggests a high packing density and, consequently, a good performance in both gravimetric and volumetric basis in adsorption-based processes. Additionally, the synthesis route that involves a hydrothermal carbonization process has shown to be the most efficient in the production of highly porous carbons (an enhancement of 49 % was recorded in the global synthesis yield). By increasing the activation temperature, substantial shortening of the operation time could be achieved without compromising pore development.

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Innovative Sensor Design for Monitoring and Mitigating the Impact of Bisphenol A on Human Health and Ecosystems

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Keywords: machine learning, peptide synthesis, biosensor, environmental contamination

Bisphenol A (BPA) is a chemical compound widely used as plasticizer in the production of plastics and resins usually found in food and beverage packaging, some medical devices, thermal paper, eyeglass lenses, and so on [1]. It is an emerging organic contaminant (EOC) that has become a significant concern due to its potential impact on both human health and ecological systems. In fact, BPA is an endocrine disruptor that can mimic or block the action of hormones, interfering with body's signalling pathways and leading to several disorders like infertility, neurological disturbances, and cardiovascular diseases. Moreover, it is related to an increased occurrence of some types of cancer. With the aim of safeguarding public health and preserving the environment, the development of accurate, sensitive, and selective detection methods for BPA becomes of outmost importance. As sensing elements for BPA detection, we propose the computational design of specific peptides employing an advanced molecular docking and machine learning approach [2]. After screening a 3.2 million pentameric peptides library, we selected those with the highest theoretical binding scores towards BPA for further synthesis. HPLC analysis showed the high purity of the peptides while UPLC-MS/MS confirmed their identity, thus validating the solid-phase synthesis method used. The selected peptides show fluorescent properties due to the presence of amino acids tryptophan, phenylalanine and tyrosine, with aromatic groups in their structure. Upon BPA binding via π - π interactions, the peptides fluorescence emission at 355 nm is modified and, therefore, they act as probes for BPA detection. This research presents an innovative sensor design that combines computational methods and advanced synthesis techniques for monitoring environmental pollutants and mitigating their harmful effects on both human health and ecosystems.

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Bio-based starch nanoparticles with controlled size as antimicrobial agents

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Keywords: Starch nanoparticles, OSA modification, controlled-size, antimicrobial.

Starch is one of the most abundant and widely used biopolymers in nature. However, native starch has some limitations, so certain modifications are used as an effective strategy to improve its properties to enable its use in specific applications. Chemical modification by esterification reactions with Octenyl Succinic Anhydride (OSA) is one of the most widely used as it could have several applications, for example as an encapsulating agent for controlled release systems. However, disrupting the starch granules at the nanoscale and using them as nanoparticles is an approach that could improve their functionality for broader applications as it would combine the advantages of both starch and nanoparticles [1]. In this context, the use of starch nanoparticles (SNPs) as biocomposite bulking agents is well known [2].

This work aimed to synthesize controlled-size SNPs by nanoprecipitation method using starches from different botanical sources. In addition, starches with different OSA modification degrees were tested, which will also allow to control the zeta potential of the surface. SNPs were characterized by their size, shape and charge using Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM). X-ray powder diffraction (XRPD) and Fourier Transform Infrared spectroscopy (FTIR) were used to analyze the structure and crystallinity of both the starch granules and SNPs.

Spherical-shape particles with size range from 54 to 108 nm were obtained with zeta potential values varying from -2 to -27 mV for the different starches and chemical modification degrees studied. It was demonstrated that size and charged tuned SNPs can be synthesized by choosing the appropriate starch type and chemical modification degree.

Therefore, the feasibility of SNPs as nanocarriers was demonstrated carrying out experiments to produce vanillin-loaded SNPs and testing their antimicrobial activity against *Escherichia Coli* (*E. coli*) with satisfactory results. Encapsulation efficiencies of 30% and loading capacities of 60% were achieved

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CO₂ hydrogenation on Ru encapsulated on silicalite: a multiscale study

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Keywords: density functional theory, microkinetic modelling, computational fluid dynamics, multiscale approach, Ruthenium

The critical levels of CO₂ emissions reached in the last decade have encouraged researchers into finding techniques to reduce the amount of anthropogenic CO₂ expelled to the atmosphere. One possibility is to capture the produced CO₂ from the source of emission or even from air (i.e., direct air capture) by different materials (e.g., zeolites, MOFs, ionic liquids, ...). Among the different usages of the captured CO₂ its conversion into light fuels as methane, methanol, formic acid, ... is essential for ensuring the long-awaited circular economy. This can be done through comprehensive knowledge and understanding of catalyst behaviour, reaction kinetics and reactor design. For this reason, multiscale approaches are essential to study the different outcomes provided at different level of simulations. In this study, starting from a previous work from our group^{1,2}, a detailed mechanism composed by 47 elementary reactions (in both forward and reverse directions) has been proposed for the CO₂ hydrogenation over Ru single atom catalyst, encapsulated in silicate (Ru1@S-1). At the microscopic level, Periodic Density Functional Theory (DFT) calculations were performed to evaluate the reactions energies and energies barriers for all the studied reactions. Then, Microkinetic Modelling (MKM) simulations have been performed, using the DFT data computed to evaluate the gas production over time at different temperatures and pressures. The analysis of the results shows that the production of CO is the main gas produced followed by formic acid and formaldehyde. At the macroscopic level, Computational Fluid Dynamics have been carried out to evaluate the best performing reactor geometry and the most appropriate temperature and pressure conditions to enhance the catalytic properties of our model, using the data obtained during the previous DFT and MKM simulations.

Acknowledgments:

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Remodelling tumor microenvironment with small molecules: synthesis of new podophyllotoxin dual target hybrids with cytotoxic and immunogenic activity.

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Keywords: Podophyllotoxin, Histone deacetylase, Topoisomerase II, Hybrid, Anticancer, Immunotherapy.

Abstract: Currently, 60 % of drugs used in cancer treatment are derived from natural sources. Their clinical application is hindered by challenges such as low bioavailability, associated toxicity and lack of selectivity. In response to these obstacles, the strategy of designing molecular hybrids as multi-target drugs has emerged as an innovative approach. The combination of various chemical entities with different activities and mechanisms of action has demonstrated to overcome disadvantages of chemotherapy [1]. In this study, the design and synthesis of new hybrids based on podophyllotoxin, a cytotoxic cyclolignan isolated from the resin of *Podophyllum emodi*, have been carried out. One of the structural components of the hybrids is podophyllotoxin, used as Topo II inhibitor [2]. Besides, considering vorinostat (an immunogenic cell inducer) as histone deacetylase (HDAC) inhibitor [3, 4], structural requirements of this compound are attached to C-7 position of podophyllotoxin scaffold. These hybrids are expected to present cytotoxic and immunogenic activity, that could restore the immune microenvironment in favor of tumor elimination.

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Flash presentations





Development of a novel chemoenzymatic synthesis of tamsulosin

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Keywords: Biocatalysis, chirality, lipases, tamsulosin, transaminases

Biocatalysis is a crucial synthetic tool to perform sustainable and environmentally chemical processes from both academic and industrial perspectives.^[1,2] This has not gone unnoticed by the pharmaceutical industrial sector, due to the ability of enzymes to differentiate between enantiomers for a determined target.^[3] This work is focused on the exploitation of biotransformations to design a chemoenzymatic route towards tamsulosin, drug used to treat symptomatic benign prostatic hyperplasia and chronic prostatitis (Figure 1).^[4]

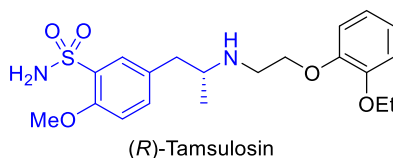


Figure 1. Chemical structure of (*R*)-Tamsulosin, highlighting in blue the fragment obtained via independent enzymatic methods.

Based on the higher biological activity of its (*R*)-enantiomer compared with the (*S*)-counterpart, the design of stereoselective routes is currently a need. Therefore, two complementary strategies have been studied, employing different biocatalyst classes. The first one is based on the use of lipases for the kinetic resolution of the corresponding racemic amine. Alternatively, the second approach employs transaminases for the biotransamination of a ketone intermediate. Finally, the coupling of the so-obtained two chemical fragments and final deprotection of the sulfonamide has been developed, obtaining the desired drug in good overall yield.

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ElectroELISA Probe: A new tool for on-site electrochemical ELISA readout of Epstein-Barr Virus serological tests

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Keywords: electrochemical probe, decentralized analysis, immunoassay, Epstein-Barr Virus (EBV), infectious mononucleosis.

The Epstein-Barr virus (EBV) is a lymphotropic γ -herpesvirus that infects over 90% of the population and can cause or contribute to the development of diseases such as infectious mononucleosis, cancer, and multiple sclerosis. The diagnosis of EBV infection is performed through serological tests, but their availability is limited, especially in remote areas, since they require suitably equipped laboratories. To facilitate access to diagnosis reducing the analysis time and, therefore, decreasing the risk of viral transmission, in this work a portable electrochemical probe that could improve and speed up ELISA readouts has been developed. This probe is based on the use of metallic pins as electrodes to create a low-cost device that offers a simple, rapid, and on-site detection, which would facilitate the implementation of ELISA test in resource-limited settings, but also boost the personalized medicine.

Therefore, the aim of this study is to design a user-friendly electrochemical cell that serves as an alternative detection tool for ELISA immunoassay, which has been applied for the diagnosis of EBV infection. Nevertheless, this device is adaptable for the rapid and decentralized diagnosis of other diseases, overcoming the current limitations of conventional serological tests.

To achieve this, different materials and modifications were evaluated [1] as cheap electrodes, resulting in an integrated electrochemical cell on a support easily adaptable to the wells of commonly used microtiter plates for immunoassays. Finally, the developed device has been applied for the determination of human antibodies against EBV, proving its potential as a low-cost, easy-to-use, and portable reader for immunoassays.

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Photo-biocatalytic deracemization of β -chlorohydrins

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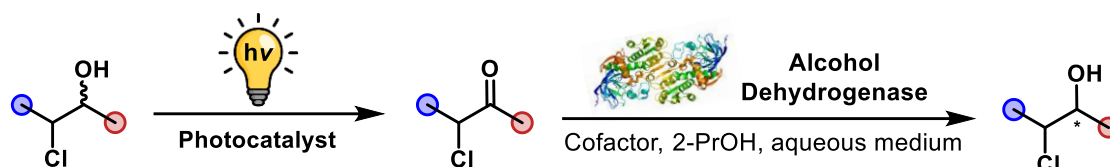
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Keywords: photochemistry, biocatalysis, cascade reaction, deracemization, chlorohydrin.

Enantiopure β -chlorohydrins are valuable intermediates in organic synthesis as chiral building blocks for obtaining biologically active compounds. In this regard, several enzymatic methods have emerged to provide chlorohydrins with high enantiomeric excess, e.g. via deracemization of their own racemic mixture.^[1,2] This process remains a significant challenge due to the inherent difficulty of the initial oxidation step. Approaches have been accomplished by using strong oxidants and metal-based catalysts. However, catalytic methodologies employing greener oxidants and milder conditions are highly appealing as competitors for large scale applications.^[3] In this context, photochemistry emerges as a promising tool.^[4]

We propose a one-pot two-step strategy for the efficient deracemization of β -chlorohydrins. In this way, the racemic β -chlorohydrin is oxidized to its corresponding ketone using an organophotocatalyst under visible light. Then, the generated ketone undergoes a stereoselective reduction catalysed by an alcohol dehydrogenase (ADH),^[5] allowing the synthesis of the desired enantiopure β -chlorohydrin.

Our approach represents a significant advancement in the deracemization of β -chlorohydrins, introducing a greener alternative for the challenging oxidation step.



Acknowledgments: Financial support from the Spanish Ministry of Science and Innovation (MCI, PID2019-109253RB-I00) and the Asturian Government (AYUD/2021/51542).

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In situ bio-H₂ production in biorefineries from syngas streams by steam reforming with integrated CO₂ capture

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Keywords: Syngas, Hydrogen, Reforming, Biorefinery, CO₂ capture

The multiple options for converting biomass into biofuels and energy carriers have boosted the development of biorefineries. Hydrogen is highly demanded within a biorefinery because it is essential for converting precursors such as bio-oils, synthesis gas, or biogas into liquid biofuels. This work focuses on the in situ production of bio-H₂ by catalytic sorption enhanced steam reforming (SESR) of gas streams, more precisely, syngas produced within a biorefinery. In this context, the effect of syngas composition on H₂ production has been evaluated using syngas mixtures composed of H₂/CO/CH₄/CO₂ representative of those typically produced in off-gas streams from thermochemical biomass conversion processes. SESR experiments were carried out in a Microactivity Reference setup (PID Eng&Tech) using a fluidized bed reactor, using a bed composed of Arctic dolomite as CO₂ sorbent together with a hydrotalcite-derived catalyst (1%Pd/20%Ni-20%Co) [1].

The results demonstrate that both yield and purity of H₂ remain constant over a CO concentration range of 10-40 vol.%, as well as over a CH₄ concentration range of 10-30%v/v. High H₂ purity values (98.4 vol.%) were obtained, which match those predicted by the thermodynamic equilibrium. The high capacity of the sorbent used to remove all the CO₂ contained in the syngas is noteworthy, showing its effectiveness in improving H₂ purity for all syngas streams evaluated. These results highlight the flexibility that “sorption enhanced” brings to the reforming process to use a wide range of syngas compositions as feedstock resulting from the conversion of multiple biomass types. The SESR process is, thus, revealed as a promising technology for the in situ production of renewable H₂ in biorefineries.

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DMPK Optimization of a Promising Anti-Alzheimer Multitarget Lead Compound

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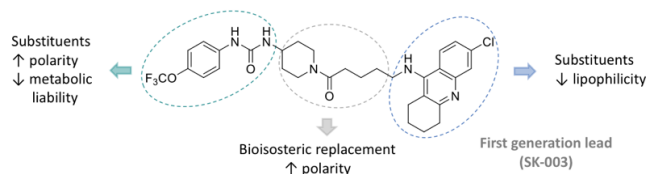
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Alzheimer's disease (AD) is an unmet medical need, and its multifactorial nature hinders the development of efficacious drugs. Thus, new therapies modulating multiple biological targets with a key pathogenic role are necessary. Our group recently reported a novel class of dual inhibitors of the enzymes soluble epoxide hydrolase and acetylcholinesterase [1], with a multitarget profile *in vitro* and beneficial *in vivo* effects against AD pathology. The lead compound showed well-balanced nanomolar potencies at both targets, good brain permeation and no cytotoxicity, but its suboptimal solubility and metabolic stability might hamper its applicability in the clinics. Here we report a lead optimization campaign, aiming to achieve more favourable DMPK properties, while retaining the high dual potencies and brain permeation of the initial lead. To this end, we have explored the effects of the introduction of different polar substituents in diverse positions of the molecule of the first-generation lead, finally emerging JM-039 as a promising anti-AD drug candidate.



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Domain-averaged Local Spin Densities

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Keywords: Spin Density, Local Spin, Quantum Chemical Topology, Molecular Domains

The partition of the expectation value of the squared electronic spin operator of a system into real space fragment contributions (local spins) is a topic that has been extensively investigated in recent years^{1,2}. Local spins are particularly important in singlet di- or polyradicals, where the spin density vanishes identically, thus precluding an easy access to the spatial distribution of up and down contributions. Projecting $\langle S^2 \rangle$ into real space domains provides a picture of the spatial distribution of this expectation value in a domain-averaged fashion that is independent of whether the spin density vanishes or not¹. The partition of space for these local spins can be arbitrarily chosen, but it is especially interesting to use atomic domains or molecular fragments, which can be obtained with real space partition methods like QTAIM (Quantum Theory of Atoms In Molecules)³.

In this work we built and implemented domain-averaged local spin densities, making use of the QTAIM partition of real space into atomic basins to: (i) draw conclusions from practical chemical examples, at different levels of theory; (ii) obtain insights into the properties of the local spin concept. The construction of local spin densities based on the theory of open quantum systems¹ is also planned.

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Photochemical Cross-Coupling of *N*-Tosylhydrazones and Boronic Acids: A Novel Strategy Towards Geminal Carboborylation Reactions

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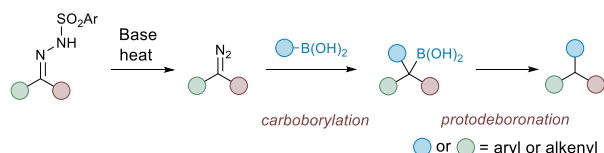
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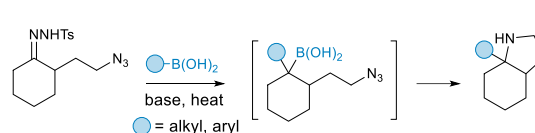
Keywords: Photochemistry, Metal-Free, *N*-Tosylhydrazone, Boronic acid, Cross-Coupling.

The reductive coupling of *N*-tosylhydrazones and boronic acids efficiently forms C-C bonds through carboborylation of a diazo compound formed in the decomposition of the *N*-tosylhydrazone.^[1] The intermediate boronic acid undergoes protodeboronation, yielding the desired coupling product (**a**). Additionally, the intermediate boronic acid can engage in further reactions, leading to C-C/C-C and C-C/C-N cascade cyclizations, resulting in the formation of two bonds on the same carbon (**b**).^[2] While alkylboronates can be isolated in thermally activated reactions, the isolation of benzyl boronates has been challenging due to their intrinsic instability. Currently, we have proven that these reactions can be driven photochemically. As the carboborylation process can be carried out under gentle conditions, the synthesis and isolation of a diverse range of benzyl boronates is enabled. This reaction offers a new approach to generate high-value boron-containing molecules ready to undergo further modification.^[3]

a) Reductive coupling of *N*-sulfonylhydrazones and boronic acids



b) C-C/C-N cascades



c) This work



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Sustainable electrocatalysts for oxygen reduction in fuel cells

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Keywords: Hydrogen, fuel cells, electrocatalyst, ORR.

Introduction: In a fuel cell, two chemical reactions take place: the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). The latter is the limiting reaction, and therefore, scientific research should focus on the optimization and development of highly efficient electrocatalysts for the ORR [1]. The objective of this work focuses on the development of new, sustainable, and efficient carbon electrocatalysts employing the sol-gel methodology assisted by microwave heating [2].

Materials and methods: The electrocatalysts were synthesized using fluoroglucinol, glyoxylic acid, and triethylenediamine (TEDA) as main reactants. The reaction was carried out in a microwave oven at 50 °C for 2 hours and 35 minutes, at atmospheric pressure in an open container. The obtained materials were functionalized by mixing them with melamine in two different ways and thermally treated at 850°C for 1 hour under an inert atmosphere.

Results: The physicochemical characterization shows that the materials are mainly spheres composed of C, H, O, and N. On the other hand, the electrochemical results obtained from the linear sweep voltammetry show that the incorporation of nitrogen functionalities increases the onset potential, and the current density, and shifts the mechanism of the reaction to a direct pathway, approaching the values of the reference material (Pt/C).

Conclusions: The carbon materials obtained exhibit promising electrochemical behavior towards the ORR, demonstrating that they can be further optimized to be competitive against the commercial reference Pt/C.

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Biogas Purification using a Pinecone Leaf-based Activated Carbon: Assessment of the Adsorption Capacity

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Keywords: Biogas, biomethane, activated carbon, adsorption.

In the current energy context, biogas as a source of biomethane is gaining significant relevance. The number of European biogas purification plants producing biomethane has doubled since 2018 [1]. One of the most widespread commercial technologies for this purpose is adsorption, which involves adsorbent materials. Replacing current commercial adsorbents with biomass-based adsorbents would reduce the carbon footprint by capturing CO₂ and promoting waste recycling and circular bio-economy.

Globally, activated carbons show good selectivity for separating carbon dioxide and high adsorption capacity at lower pressures. This study addresses the performance in separating CO₂/CH₄ mixtures on activated carbon prepared from pinecone leaves (PCL), previously characterized by our research group. Experiments were carried out in a laboratory-scale fixed-bed system at a temperature of 30 °C and different partial pressures of CO₂ and CH₄.

The results obtained from the breakthrough curves and pressure swing adsorption (PSA) cyclic tests were compared with those previously obtained for other activated carbons and commercial adsorbents. Breakthrough curve data translate into maximum adsorption capacity, whereas cyclic tests evaluate the dynamic performance under more realistic non-equilibrium conditions. The adsorption capacity was comparable to commercial activated carbons in the pressure range between 1 and 10 bar [2], reaching values between 2.4 and 4.5 mmol g⁻¹ for CO₂ and 1 and 1.5 mmol g⁻¹ for methane in CO₂/CH₄ 50/50 volume mixtures. Based on these results, PCL is a very promising activated carbon candidate for implementation in biogas purification through adsorption.

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Photocatalytic oxidative cleavage of styrenes followed by carbonyl bioreduction towards stereoselective alcohol synthesis

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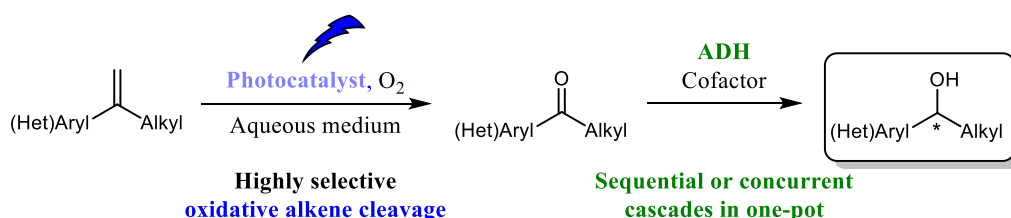
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Keywords: photocatalysis, oxidative cleavage, alcohol dehydrogenase

Photocatalysis has recently emerged as a powerful tool towards the synthesis of highly valuable organic compounds in a straightforward manner and under mild reaction conditions. Thus, light-driven chemical transformations can be easily combined with enzymes, giving rise to photobiocatalytic processes.^[1]

The chemocatalytic photo-induced oxidative alkene cleavage has been previously described under aerobic conditions in organic and aqueous media,^[2-4] usually bearing the olefin directly linked to aryl systems and leading to the formation of the corresponding ketones. Herein, we have explored the combination of a photocatalytic step with the use of alcohol dehydrogenases (ADHs) producing optically active 1-(het)arylethanol, which are intermediates for the synthesis of valuable compounds with pharmaceutical applications.^[5] A sequential photobiocatalytic approach is presented, where the light-driven oxidative cleavage of the C=C bond of a series of alkenes is followed by a bioreduction step using stereocomplementary ADHs. Interestingly, the one-pot concurrent cascade was also feasible for some specific substrates.



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Addition of nanoparticles to lightweight concrete for CO₂ capture

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Keywords: concrete, zinc, titanium, nanoparticles, single particle-ICP-MS

The addition of metallic compounds in their nanoparticulated form are part of a new generation of more sustainable construction products. Titanium dioxide (TiO₂ NPs) and zinc oxide nanoparticles (ZnO NPs) are two of the most prominent species that can be used for this purpose [1]. Their role as catalyzers of carbon dioxide (CO₂) capture is pivotal in the development of more environmentally friendly construction materials like light weight concrete (LWC). Moreover, in this work, ZnO is obtained as a byproduct in the zinc industry. Thus, its use contributes to develop a model of circular economy.

This presentation will show the application of ICP-MS in the single particle analysis mode (SP-ICP-MS) to characterize TiO₂ and ZnO NPs as concrete additives. After proper characterization of the starting material, the nanoparticles will be incorporated to different mixtures of concrete to study the resulting material, both in terms of composition and homogeneity and also in terms of mechanical properties and CO₂ capture capacity [2].

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Novel multitarget inhibitors with amyloid antiaggregating activity to treat Alzheimer's disease

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Alzheimer's disease (AD) is the leading cause of dementia worldwide. It has a multifactorial nature, with contributions of various etiopathogenic mechanisms in its onset and progression. In this context, multitarget drug design is being widely used to modify several disease mechanisms with a single compound.[1] Among the multiple proposed pathogenic factors, there are 3 that may be interrelated: neuroinflammation, cholinergic deficit and protein aggregation. In this light, we envisaged: 1) addressing neuroinflammation by inhibiting the enzyme soluble epoxide hydrolase (sEH) thus increasing the levels of EETs, which are endowed with anti-inflammatory effect; 2) increasing acetylcholine levels through acetylcholinesterase (AChE) inhibition, thereby rescuing the cholinergic deficit; and 3) with the rational design of these dual inhibitors inhibiting additionally the spontaneous aggregation of amyloidogenic proteins.[2] In this work, we describe the first class of inhibitors of sEH and AChE with amyloid antiaggregating capacity, which were designed by connecting a sEH and an AChE inhibitor pharmacophores through a suitable linker. The resulting hybrids exhibit increased potency on sEH and AChE compared to the reference sEH and AChE inhibitors, respectively, with subnanomolar or single-digit nanomolar IC₅₀ values, and significant beta-amyloid and tau antiaggregating activity, with percentages of inhibition above 50% at 10 μM concentration. Strikingly, some of these compounds can also inhibit the aggregation of TDP-43, a protein involved in several neurodegenerative diseases, including AD and amyotrophic lateral sclerosis, among others. In addition, most of them are non-neurotoxic (SH-SY5Y cells) at 100 μM, can cross the blood-brain barrier (PAMPA-BBB assay) and display moderate aqueous solubility and microsomal stability. Pharmacokinetic and efficacy studies in a mouse model of AD with a lead compound are in progress, to further assess its potential as a disease-modifying anti-AD drug candidate.

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Unveiling electron distributions in the real space

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Keywords: Electron Distribution Functions, Chemical Bonding, Quantum Chemical Topology.

Electron Distribution Functions (EDFs) serve as a valuable tool for the comprehensive exploration of fundamental tenets within the domain of chemical bonding theory. This includes the intricate examination of phenomena including electron pair sharing, charge transfer, or multiple bonding, achieved through a rigorous scrutiny of the statistical attributes inherent in multivariate electron number distribution functions [1]. Adhering to the principles set forth by Quantum Chemical Topology (QCT), EDFs are commonly deployed within the Quantum Theory of Atoms in Molecules (QTAIM) partition framework. This application facilitates the partitioning of real space into distinct basins associated with individual atoms. The Electron Localization Function (ELF), in turn, delimitate the real space into regions corresponding to Lewis entities, namely lone pairs, chemical bonds, and atomic cores.

While this conventional approach is effective for characterizing chemical bonding and maintaining essential concepts like atomic contributions and electron pair sharing, there is a desire to further refine the spatial analysis. Our study takes a step forward by employing EDF analysis at the intersection of ELF and QTAIM basins. This innovative approach aims to discern the contributions of each atom to the electron pairs associated with bonding regions in the molecular regime. Our work focuses on the study of a series of hydrides, AH_n (where A is a representative element of rows 2 to 4). By using such approach, classical and chemically soundly concepts (such as the electronegativity) have been recovered from probabilistic perspective provided by quantum mechanics, and the chemical bond within the systems have been thoroughly characterized by dissecting Lewis entities into atomic contributions [2].

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New Ru (III) NAMI-type complexes with anticancer activity

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Keywords: metallodrugs, ruthenium (III) complex, chemotherapy, antimetastatic.

Since the discovery of cisplatin as an anticancer drug, platinum (II) complexes are the most widely used chemotherapeutic agents,¹ but drug resistance as well as severe adverse effects derived from their high cytotoxicity and low selectivity appear as the main drawbacks of these drugs. Moreover, more than 90% of cancer death results from metastasis.²

For these reasons, ruthenium-based complexes are emerging as promising alternatives, as they present mechanisms of action different from the platinum ones.³ Specially, Ru (III) NAMI type complexes, which not only present lower toxicity but also have great antimetastatic activity, being NAMI-A the first Ru (III) anticancer compound to be studied in humans and has reached phase II clinical trials.⁴

For all that, in this work we reported the development of a library of new NAMI type Ru (III) complexes with a high variety of functional groups. Moreover, the *in vitro* cytotoxicity of the synthesized Ru-complexes was tested through MTT assays in three cancer cell lines. The different functional groups in the Ru-complexes not only allow further modifications and distinct reactivity, but we have also demonstrated that the IC₅₀ and selectivity drastically change with the counterion and moieties of the ligands, obtaining new promising results for the chemotherapeutic anticancer strategy.

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Microwave synthesis of new co-polypyrrole-polyketone for anion exchange membranes

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Keywords: Anion exchange membranes; microwave-assisted synthesis; polyketone; Paal-Knorr reaction

The Paal-Knorr reaction is a well-known cyclization reaction of the 1,4-diketones. Over the almost one hundred and fifty years after its discovery, it has been widely used with different applications and still attracts the interest of the researchers. Our group is pioneering its use on aliphatic polyketone to obtain ion exchange polymers for electrochemical applications [1-3]. It seems to be a very promising route thanks to the facile synthesis and the low cost of the starting materials. Here we present the synthesis and characterization of new polymeric anion exchange membranes (AEMs) based on a polypyrrole-polyketone backbone and pyridinium pendant groups obtained from a commercial and inexpensive terpolymer polyketone (PK). Different degree of functionalization of the 1,4-diketonic units were obtained using 3-(aminomethyl)pyridine in different amine/PK molar ratio. Moreover, in this work we present the drastic reduction of the reaction time, investigating an alternative and greener heating source, microwaves. The anion exchange version of the membranes was obtained by simple methylation to obtain the iodinated form and by ion exchange the hydroxylated form. The molecular structure, thermal and conductive properties of the membranes were studied in order to shed light on conduction mechanism and to lead the way to their further optimization for the possible application in electrochemical devices.

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Novel *helico*BODIPYs as CPL-active small organic molecules

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Keywords: *Organic dyes; BODIPYs; Photonic materials; CPL*

Circularly polarized luminescent (CPL) materials based on small organic molecules (SOM) are considered the next generation of photonic materials.¹ The development of tunable and highly efficient CPL-active SOMs, however, remains challenging. Boron dipyrromethene (BODIPY) chromophores offer a potential avenue for enhancing CPL emission efficiency, and molecular helicity is usually utilized to augment g_{lum} (luminescent dissymmetry factor), representing valuable strategies to improve CPL brightness in CPL-active SOMs.² The *helico*BODIPYs from de la Moya's group embody these features while involving synthetic accessibility, establishing them as compelling CPL-active SOM.^{3,4} *Helico*BODIPYs consist of two BODIPY chromophores connected by a short C_2 -symmetric spacer, enabling BODIPY-BODIPY intramolecular charge transfer (ICT), crucial for CPL activity and its modulation.^{3,4} We present the synthesis (using the methodology established by de la Moya for prior *helico*BODIPYs)^{3,4} and preliminary photophysical characterization of unprecedented *helico*BODIPYs comprising two or four BODIPY units connected by unexplored short C_2 -symmetric spacers based on marketed enantiopure diols or tetraols. They exhibit promising photophysical and chiroptical behavior in solution, contributing to advancing controlling of ICT and modulating CPL activity.

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Use of life microorganisms, fibre and polyphenols as possible dietary targets for microbiota modulation at early life stages

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Keywords: Live microorganisms, fibre, polyphenols, microbiota, children

Introduction: The intake of fibre and polyphenols among other dietary components, such as live microorganisms (LMO), can modulate the gut microbiota. However, no studies to date have integrated all these variables. **Objective:** To evaluate the intake of fibre, polyphenols and LMO in a cohort of children from 6 months to 4 years and to study their impact on faecal microbiota. **Methods:** Longitudinal study in 58 children across age: 6 months (n=57), 12 months (n=58), 24 months (n=36), 36 months (n=43), and 48 months (n=15). Diet was recorded by food frequency questionnaire. The different classes of fibre from Marlett et al. [1], and (poly)phenols from Phenol-Explorer [2]. Foods were classified according to their LMO content based on Marco et al. [3]. Faecal microbiota were determined by Illumina 16S rRNA gene-based analysis **Results:** High intakes of LMO, fibres and polyphenols at 6 and 36 months were significantly associated with higher levels of *Veillonella*, that have shown anti-inflammatory features [4]. The intake of fibre, hydroxycinnamic acids and furanocoumarins at 12 months were significantly positive correlated with the levels of *Coriobacteriaceae* while the intakes of pectin (soluble and insoluble), hydroxybenzoic acids and lignans at 24 months were significantly positive correlated with the levels of *Peptostreptococcaceae*. The intake of polyphenols at 24 months and of fibres at 36 months were significantly positive associated with *Prevotellaceae* levels. This family has shown to be reduced in diseases as autism and attention deficit/hyperactivity disorder [5]. The intake of insoluble fibres at 48 months was significantly positive correlated with *Ruminococcaceae* levels. This family produces important amounts of butyrate, a SCFA related with a positive impact on gastrointestinal health [4]. **Conclusion:** Significant changes in faecal microbiota have found according to the intake of LMO, fibres and polyphenols. These compounds could be used as dietary targets for microbiota modulation at early stages.

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Metal-Doped Carbon Aerogels As Electrode Materials For Non-Enzymatic Glucose Sensors

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Keywords: Aerogels, electrochemistry, sensors, glucose.

Introduction and research purpose: New developments in materials science have enabled the technological advancement of non-enzymatic electrochemical glucose sensors, that allow an easy and quick diagnosis and monitoring the glucose levels in case of diabetes disease. Nanomaterials with high purity, great chemical stability and porosity, and exceptional electrical conductivity are the most suitable electrochemical sensing interface for this application. Specifically, in this work, metal-doped carbon aerogels were obtained and tested as potential electrode materials for non-enzymatic electrochemical sensors for glucose detection.

Materials and methods: Carbon aerogels were synthesized by microwave heating at 85°C for 3 hours. After synthesis, the materials were dried in an oven or a lyophilizer, and subsequently, carbonized. The incorporation of metals (5% w/w) in the carbon supports was carried out in two different ways: *ex-situ* (wet impregnation post-treatment) and *in-situ* (adding the metal to the precursor solution). The electrocatalysts prepared *ex-situ* were also subjected to a reduction process. All materials were characterized in terms of their chemistry, porosity, and electrical conductivity, as well as electrochemically by modifying the surface of carbon screen-printed electrodes by drop casting.

Results and conclusions: The electrocatalysts prepared have a percentage of porosity between 75% (carbon aerogels) and 95% (graphene aerogels) and the electrical conductivity in graphene aerogels (1000 S m^{-1}) is eight times higher than in carbon aerogels. This synergistic effect of high porosity and high conductivity in graphene aerogels is reflected in the sensitivity analyzed using Ni-doped graphene aerogels, which are notably higher than those without graphene in the structure, with values of 55 vs. $3 \mu\text{A mM}^{-1} \text{ cm}^{-2}$, respectively. Moreover, Ni-doped graphene aerogels prepared *ex-situ* show higher electrochemical sensitivity than graphene aerogels prepared *in-situ*, 55 vs. $34 \mu\text{A mM}^{-1} \text{ cm}^{-2}$, respectively, due to the higher percentage of accessible nickel on the surface. Thus, it appears that a good combination of high porosity, electrical conductivity and available Ni active centers are necessary characteristics for the development of efficient glucose sensors.

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Determination of proteins in hypoxic Müller glia cells by single cell ICP-MS: The use of DNA intercalators for enhanced cell detection

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Keywords: Single cell ICP-MS, Metal nanoparticles, DNA intercalator, Müller glia cells, Hypoxia

Cell populations in all biological systems are well known for their heterogeneous nature. Cellular samples can be analysed by elemental mass spectrometry (i.e., ICP-MS) after digestion of the cell, providing information of the whole population as an average. However, the large cellular heterogeneity within a single isogenic culture requires specialized techniques that allow the analysis of cells as individual entities.

In this vein, determination of target analytes in single cells can be successfully achieved employing single cell (sc) ICP-MS. Additionally, the combination of sc-ICP-MS with immunocytochemistry makes possible to determine both endogenous elements and proteins in individual cells. For this aim, the cellular samples are subjected to an immunoassay using an elemental label (e.g., metallic nanoparticles). Concerning the quantitative study of intrinsic elements (like Fe, Ca or Zn), they should be monitored not only as target analytes but also to assure cell integrity and to confirm the recognition of the employed immunoprobe. However, as endogenous elements are in low concentrations within individual cells, their determination is often limited by the sensitivity of sc-ICP-MS.

In this work we have studied a DNA-intercalator containing Rh to significantly enhance sensitivity in cells detection by sc-ICP-MS in Müller glia cells (MIO-M1). We evaluated MIO-M1 cells subjected to an atmosphere with a low concentration of O₂ (hypoxia), comparing them to a control state (normoxia). In addition to the use of the DNA-intercalator to improve cell detection, metal nanoclusters (AuNCs and IrNCs) were employed to label specific antibodies targeting proteins related to hypoxia (HIF-1 α and VEGF) in MIO-M1 cells.

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3-Nitro-2*H*-chromenes: useful synthons in photoredox Giese reaction

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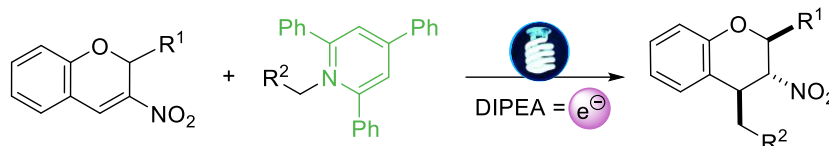
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Keywords: 3-nitro-2*H*-chromenes, photoredox, oxa-Michael Henry domino reaction.

Chromenes derivatives are ubiquitous in nature and possess a broad of biological properties.¹ 3-Nitro-2*H*-chromenes are of particular interest, they are useful building blocks for constructing diverse scaffolds in the pharmaceutical industry.² They are easily available and there are several synthetic procedures described in the literature.³

Herein we describe the oxa-Michael Henry domino reaction of salicylaldehydes and nitroalkenes and the photoredox addition of benzyl radicals to the resulting 3-nitro-2*H*-chromenes to afford 4-alkyl-3-nitro-2-arylchromanes in moderate yields and high diastereoselectivities (Scheme 1).



Scheme 1. Synthesis of 3-nitro-2*H*-chromenes and photoredox radical Michael addition.

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Hydrolysed sewage sludge as biosorbent for methylene blue removal

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Concerns arise from the substantial volume of sewage sludge generated as a primary by-product of wastewater treatment, which is estimated to be approximately 13 million tons of dried solids per year. For this, various methods are employed for its management and repurposing, with the thermal hydrolysis process being one such method. This process disintegrates sludge flocs, releasing diverse compounds like proteins, humic-like substances, and carbohydrates into the liquid phase of sewage sludge, opening up various applications [1]. Despite this, a residual dry solid fraction remains after thermal hydrolysis, suggesting additional usability.

This study aims to investigate the potential utilization of the solid fraction derived from post-treatment sewage sludge for the adsorption of methylene blue. The research involves the characterization of both the liquid fraction, focusing on biomolecules, and the solid fraction, examining suspended volatile solids, composition, texture, structure, and morphology. This analysis was conducted on thermally treated sludge samples subjected to various temperatures ranging from 125°C to 185°C for 1h.

The results indicate that elevated temperatures result in heightened biomolecule solubilization, attributed to increased kinetic energy of molecules [2], leading to floc rupture, reduced volatile matter, expanded surface area, and macropore formation. Conversely, the adsorption of methylene blue decreases with rising thermal hydrolysis temperatures, which is associated with the organic matter content and functional groups [3]. Subsequently, the material treated at 125°C was selected for further adsorption studies due to its higher adsorption capacity. Optimal adsorption conditions were determined to be a pH of 12 and an adsorbent concentration of 1000 mg/L, with the Langmuir model ($R^2 = 0.998$) demonstrating the best fit and revealing a maximum adsorption capacity (q_{max}) of 397 mg/g. This research thus contributes novel insights into the management of residual solids following the thermal hydrolysis of sewage sludge.

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LA-ICP-MS for quantitative distribution of (Bio)markers in Breast Cancer

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Keywords: Laser ablation, Mass spectrometry, Bioimaging, Biomarkers, Cancer.

Essential trace elements possess important effects, as constituents of various enzymes, in a huge number of biological processes. Changes in metals concentration may play a significant role in cell dysfunction and proliferation, including the development and progression of cancer [1]. Zinc, in particular, has been of great interest, because it is a catalytic component of Matrix Metalloproteinases (MMPs) which may be inhibited by their Tissue Inhibitors (TIMPs) through their binding to the catalytic Zn cofactor. These proteins are involved in the pathogenesis of Breast Cancer and variations in the expression of MMPs and TIMPs has been proposed as new prognostic biomarkers in this disease. It has been found that overexpression of TIMP2 is related to poor prognosis and metastasis in different types of cancer [2].

For this purpose, a methodology for quantitative bioimaging of metals (Fe, Cu, Zn and Sr) in breast cancer tissue has been developed by Laser Ablation - Inductively Coupled Plasma – Time of Flight (LA-ICP-TOF). Gelatine matrix-matched standards were used for the external calibration. The developed methodology was applied to healthy, non-metastatic and metastatic tissues. Differences in the levels of essential trace elements related to metalloproteins (Fe, Cu and Zn) were found between healthy and breast cancer groups. Also, alterations were observed for exogenous elements like Sr.

Moreover, the quantitative distribution of TIMP2 in breast tissue was carried out by an immunoassay in combination with LA-ICP-MS. The specific antibody was conjugated with Europium. The BC tissues were incubated with this antibody and the TIMP-2 distribution was determined by the Europium signal and an external calibration with gelatine standards. Finally, differences between healthy, non-metastatic, and metastatic samples were evaluated.

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Modular synthesis of new BODIPY dyes with strong NIR emission properties

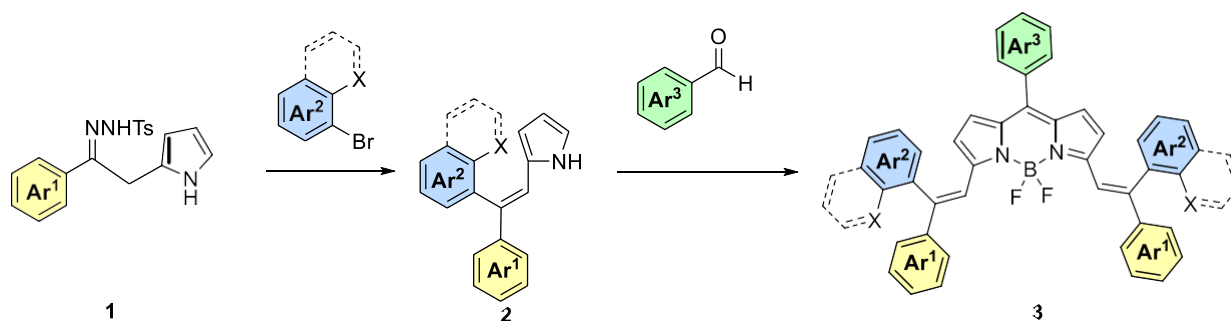
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Keywords: BODIPY dyes, cross.coupling, *N*-tosylhydrazone,

A novel synthetic route towards highly conjugated BODIPY derivatives is reported. Starting from pyrrole and α -chloro-*N*-tosylhydrazones the new pyrrole substituted *N*-tosylhydrazones **1** were obtained. Pd-catalyzed cross-coupling reaction with aryl bromides provides diarylvinyldiarylpyrroles **2** with total diastereoselectivity.¹ Then, condensation with aldehydes led to the highly conjugated BODIPYs **3**. This synthetic route showcases high modularity, allowing the preparation of unprecedented diverse dialkenylBODIPYs with different substitutions at Ar¹, Ar² and Ar³, enabling the tuning of the photophysical properties. Importantly, the structures prepared show strong emission properties in the red and near IR regions, depending on the specific substitutions.²



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[2] Álvar Serrano-Pindado,¹ Manuel Plaza,¹ Carlos Valdés^{1*} **2024**, ongoing.



Preparation of starch films added with lactobionic acid for antibacterial application

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Keywords: lactobionic acid, antibacterial activity, starch film, cheese

Due to its demonstrated biological properties, lactobionic acid (LB) was gaining interest and could constitute a promising food preservative. This work consists of the evaluation of antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* as a model of foodborne pathogens. The minimum inhibitory concentration, determined by the microplate dilution method, was estimated to be 12.5 mg/mL. By direct incorporation into the nutrient medium, LB at MIC and 1/2MIC reduced *E. coli* cell growth by 0.7 and 8 log/mL, respectively. *S. aureus* was more sensitive with reductions of 3.7 log/mL for 1/2 MIC and 7.3 log/mL for MIC. Subsequently, films based on starch and LB were prepared at different concentrations and their inhibitory effect was determined. A limited inhibitory effect was recorded with the film containing LB at 1/2 MIC in liquid broth, while a considerable effect was obtained with the film at 1 MIC. The latter demonstrated effectiveness in preserving cheese against both germs under standard refrigeration conditions.



Design and optimization of an immunoassay for GFAP determination as biomarker for differential diagnosis of stroke

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Keywords: stroke, diagnosis, GFAP, immunoassay, ELISA.

Stroke is the third leading cause of death in the world, and its differential diagnosis between ischemic and hemorrhagic strokes, which require different treatments, involves time-consuming techniques based on brain imaging, only available in hospitals. The administration of the suitable treatment in the shortest time is vital for the patient's outcome, but the current diagnostic techniques slow down the process. Therefore, it is crucial to develop novel tools such as quick biomarker-based tests, that provide a quantitative result allowing a faster differential diagnosis and, therefore, a rapid application of the needed treatment that leads to an improvement of both survival and quality of patient's life.

In the context of stroke biomarkers, GFAP (glial fibrillary acidic protein) is a very interesting marker for the discrimination of stroke subtypes since, being abundantly present in astrocytes, in case of brain tissue destruction, it will be released into the blood. This molecule is released first into the bloodstream in the case of a haemorrhage, but later on after the disease onset in the case of an ischemic stroke. Thus, this difference has been thoroughly studied as a differential biomarker of stroke subtypes in blood and nasal exudate [1].

For this purpose, a one-step ELISA (enzyme-linked immunosorbent assay) immunoassay has been designed and optimized for the detection of GFAP protein. This work focused on finding a suitable pair of antibodies for the detection of human GFAP whose detection antibody is conjugated to HRP (horseradish peroxidase), assessing different antibodies and conjugation strategies. The developed immunoassay showed promising results for its potential integration into quick diagnostic tests for the fast and accurate differential diagnosis of haemorrhagic and ischaemic stroke.

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Effect of operational conditions on the entrapment of microplastics (MPs) in secondary sewage sludge

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Keywords: Wastewater treatment plant, sewage sludge, microplastics, entrapment, environmental pollution

During the wastewater treatment, usually carried out in urban wastewater treatment plants (WWTP), an important part of the microplastics (MPs) (around 95%) ends up in the sewage sludge. Nevertheless, to date, there is very little information on how operating conditions affect the removal of MPs by entrapment in sewage sludges. Literature have reported sewage sludges with MP concentrations very different, from 400 to 170,000 particles per kg (dry weight). The objective of this study was to analyze the effect of different physical-chemical parameters (use of coagulant/flocculant agents, sludge concentration and degree of mixing) on the efficiency of MPs retention in secondary sewage sludges. MPs used for the experiments were collected from secondary sewage sludges supplied by a municipal WWTP. After purification, MPs were recovered and characterized, finding that the most abundant form was fibers (61%), the majority of MPs were within the size range 250 - 500 μm and the most frequent colors were black and blue, with 41% and 24%, respectively.

Entrapment experiments were carried out using a Jar-Test apparatus, testing different operational conditions. Without adding chemicals, the maximum MP retention efficacy, 63%, was obtained with a concentration of 50 g of sludge per L of water. When, coagulant and flocculating agents were employed, the percentage of MPs retention in sewage sludge increased till values of 82% and 70%, respectively. Comparing the MPs removed by entrapment in the sludge particles, a relative homogeneity was obtained related to the size, shape and colors, independent on the conditions used for the experiment.

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Characterization of human milk exosomes: pasteurization effects

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Keywords: human milk, exosomes, pasteurization, neonatal health

Human Breast Milk (HBM) is the ideal food for infant nutrition, which contains all macro- and micro- nutrients necessary for the correct development of the newborn. Moreover, HBM has many bioactive components as antibodies, chemokines, cytokines, growth factors, hormones immunoglobulins and extracellular vesicles (EVs). Exosomes are nano-size extracellular vesicles of great interest that transport biologically active compounds (genetic material, proteins, and lipids) and act as cellular messengers transporting material and information to other cells, where they mediate in multiple processes with important health benefits [1]. For these reasons, the World Health Organization (WHO) recommend exclusive breastfeeding for feeding newborns and especially premature newborns. Banked Human Milk (BHM) is the best alternative feeding preterm infants when maternal milk is not available or is insufficient. BHM is pasteurized to mitigate infectious risks. However, Pasteurized Donor Breast Milk (PDBM) can lose bioactive and immunological properties [2]. Therefore, it would be of great interest to evaluate the impact of pasteurization on milk exosome integrity.

The aim of this study is the characterization (distribution of sizes, concentration) and composition (proteins, essential metals, and miRNA) in human milk exosomes. Several methods, including transmission electron microscopy (TEM), nanoparticle tracking analysis (NTA), BCA protein assay, size exclusion chromatography (SEC), dynamic light scattering (DLS) and flow cytometry, have been developed for the characterization of milk exosomes. The methodologies developed will be applied to characterize HBM exosomes at different stages of lactation (colostrum, transitional and mature milk) and to evaluate the impact of pasteurization on its characteristics.

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Synthesis and reactivity of 2-(aminomethyl)BODIPYs. Significance in BODIPY functionalization chemistry

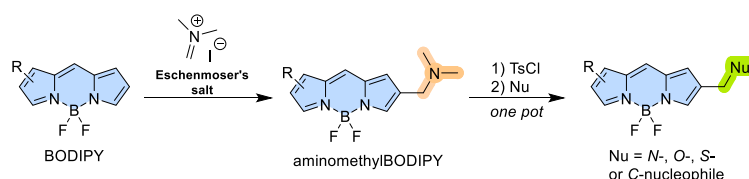
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Keywords: Organic dyes, BODIPYs, BODIPY chemistry, fluorescence

BODIPYs (boron dipyrromethenes) constitute a well-known family of organic dyes extensively utilized in various photonic applications and tools related to Energy and Health, such as active components in dye lasers or fluorescent probes for bioimaging [1],[2]. This widespread use is due to the excellent photophysical properties of the BODIPY chromophore [3] and the versatility it offers for modulation through well-established BODIPY chemistry [4]. Specifically, functionalization at the pyrrolic β -position of BODIPY is commonly achieved either through electrophilic aromatic substitution or via Pd-catalyzed C-C coupling [4]. In this context, we present a novel general method for the easy and efficient functionalization of BODIPYs at said pyrrolic position using readily accessible nucleophilic reagents. This method involves the straightforward preparation of a 2-(aminomethyl)BODIPY (see Figure 1), serving as intermediate for subsequent functionalization with the selected nucleophilic reagent. A key added advantage of this method is that the introduced moiety is electronically isolated from the BODIPY chromophore by a methylene group. Consequently, this functionalization can be employed to easily tag nucleophiles with a specific BODIPY (e.g., a fluorescent one in a specific colour region) or to confer additional properties (e.g., water solubility, chemical reactivity or biospecificity) to an already photophysically-optimized BODIPY dye for its fine-tuning towards a final photonic use.



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Posters





Hydroiodination of internal alkynes promoted by acidic Deep Eutectic Solvents

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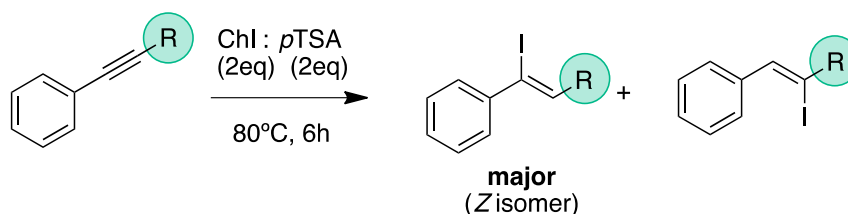
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Keywords: Deep Eutectic Solvents, Hydroiodination, Alkynes.

The use of deep eutectic solvents (*DESs*) is an emerging alternative to traditional solvent chemistry,^[1] allowing to perform chemical transformations of interest with the advantage of using mild reaction conditions in a more sustainable way. Specially, Lewis- or Brønsted-type acidic *DESs* have been capable to display key roles in organic synthesis, being recently published by our research group both the Meyer-Schuster rearrangement^[2] as well as the hydration^[3] of terminal alkynes promoted by Lewis *DES*.

Herein, we present the reactivity of different acidic *DESs*, using both Brønsted and Lewis acids and an iodide source in order to promote the hydroiodination of internal alkynes. In the case of using ChCl:*p*-TSA mixture (ChI:*p*-TSA, Scheme 1), the corresponding iodovinyl compounds were obtained with high yields (up to 97%) and excellent selectivities (majority anti-Markovnikov and (*Z*)-isomer)



Scheme 1. Synthesis of iodovinyl compounds promoted by ChI:*p*-TSA mixture.

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Rapid and non-invasive sensor for dual optical detection of biogenic amines in food

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Keywords: Metal organic-framework, Color, Fluorescence, Biogenic amine, Food safety

NanoMOFs (metal organic frameworks) are crystalline nanoparticles composed of ions of a metal or a cluster connected via organic ligands that can be used in a wide range of applications. Their porous structure, large surface area, modifiability and luminescent properties have remarkably increased their applications in sensor designs [1]. These nanomaterials have been introduced in the food industry due to their low toxicity, efficiency in the production of food packages, and improvement in food preservation. Other alternatives in which these nanomaterials can play an important role are those based on the development of new methodologies for Food Safety and Quality controls. Some compounds, that appear because of the metabolic activities of microorganisms in food are Biogenic Amines (BAs). Their presence in non-fermented foods is usually undesirable and is related to microbial spoilage. The presence of these BAs in high concentrations can produce severe toxicological effects in humans [2]. The best methodology to detect BAs in food should be a fast, simple and non-invasive procedure, that does not destroy the sample, allowing the analysis in the production line or even incorporating the sensors in the packaging. [2].

This research work proposes the use of nanoMOFs as colorimetric and luminescent indicators of BAs presence in food samples. For this purpose, the changes in luminescence properties of the fluorescent copper MOF when exposed to different amines, including cadaverine and putrescine, have been studied. The optical behaviour of the nano MOFs varies depending on the amine, and a loss of fluorescence is observed at different speeds, making possible the design of a "turn off" and non-invasive fluorescence sensor. PVC and nanoMOF membranes were designed and after exposing these membranes to different BAs colorimetric and luminescent changes were observed going from the characteristic green colour of the MOF to yellowish and brown colours.

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Starch nanocolloids: fine-tuned for biofunctional applications

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Keywords: Starch, micelles, liposomes, niosomes, targeted drug delivery.

Starch, a naturally abundant, biodegradable and biocompatible polysaccharide, has attracted increasing attention for its nanoparticles (SNPs) due to their advantageous properties: including high surface area to volume ratio, potential for surface functionalisation and biocompatibility [1]. Despite these, SNPs have a tendency to aggregate, which poses a significant challenge [2]. This problem can be mitigated by encapsulating SNPs in nanocapsules, such as micelles, vesicles or lipid-polymer hybrid nanoparticles. The versatility of starch, influenced by its botanical source or chemical modification, adds to the adaptability of these nanocapsules.

This study focuses on the synthesis of colloidal systems encapsulating quinoa starch nanoparticles and their functionalisation. Four different colloidal systems were formulated, all characterized by surface functionalization with carboxylic acid groups: polymeric micelles, liposomes and niosomes composed of phospholipids or non-ionic surfactants. Different encapsulation methods were studied to optimise the synthesis of these sustainable nanocolloids.

Characterization by dynamic light scattering (DLS) determined size and surface charge, while transmission electron microscopy (TEM) assessed morphology and monodispersity. Fourier transform infrared spectrometry (FTIR) was used to analyze the molecular structure.

These systems have potential as nanocarriers for drug delivery or for bioconjugation on their surface with specific compounds (proteins or ligands). This opens up avenues for applications such as targeted drug release or the development of biosensors.

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Metal-Free Visible-Light-Mediated Cyclopropanation of *gem*-Bromonitroalkenes.

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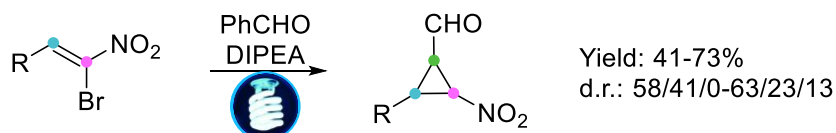
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Keywords: Cyclopropanes, photochemistry, nitroalkenes, drug discovery.

Cyclopropanes are small, rigid structures that play a key role in the biological activity of organic molecules. From the perspective of developing new drugs, these structures are highly interesting as they provide both rigidity and three-dimensionality, two essential properties for modulating the mode of action of a bioactive molecule with its receptor.^[1]

Cyclopropanes are commonly synthesised through [2+1] cycloaddition reactions, which, are usually carried out using transition metals as catalysts.^[2] Other transition metal-free cyclopropanation have also been reported in the past few years. However, most of the cyclopropanation strategies reported to the date are not sustainable in terms of environmental impact. Connected with the clear benefits of photochemistry for sustainability, cyclopropanation under visible light irradiation has attracted much attention recently.^[3]

In this context, we describe herein a direct method to access 1-formyl-2-nitrocyclopropanes from readily available *gem*-bromonitroalkenes and *N,N*-diisopropylethylamine (DIPEA) using benzaldehyde as photoinitiator.



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Comparison of endogenous and exogenous cell markers for single cell analysis using inductively coupled plasma mass-spectrometry (ICP-MS)

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

In single-cell inductively coupled plasma-mass spectrometry (ICP-MS) studies, phosphorus is commonly used as an internal cellular marker due to its abundant presence in all cells. It is a constituent of various cellular components, including DNA, RNA or phospholipids present in the cell membrane among others [1]. However, measuring this element using single-cell ICP-MS is challenging due to both the polyatomic interferences and the high background caused by phosphate buffers, which are commonly used in most biological protocols. As a result, alternative elements have been explored as potential cell markers. Constituent elements like iron or copper presents similar issues. Nevertheless, the use of external cell markers, particularly heavy metals, are gaining popularity due to their excellent sensitivity for detection by ICP-MS, together with minimal biological and environmental backgrounds.

This study focuses on investigating the application of an iridium compound as a cell marker for single-cell ICP-MS analysis. This compound is a cationic nucleic acid intercalator containing iridium with a natural isotope composition (¹⁹¹Ir and ¹⁹³Ir). When cells are treated with this compound, it intercalates within the cellular nucleic acid. The detection of both stable isotopes allows the identification of the nucleated cells. For this purpose, the iridium cationic intercalator will be added to previously fixed and permeabilized human ovarian cancer A2780 cells. The detection of cells using endogenous phosphorous and iron or the exogeneous iridium as a cell marker will be compared and evaluated as well as the sample conditions before measurement. The iridium labelling of cells will be quantitatively characterized in relation to the phosphorous and iron content in individual cells, with a specific focus on the intercellular variability.

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Bionenergy from industrial food wastes by means of Pyrolysis Processes

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Keywords: Corn cobs waste, Macroalgae waste, Pyrolysis Technologies, Biofuels, Bioenergy.

The lack of energy resources and global warming of the earth, caused by the increase of CO₂ in the atmosphere due to the use of fossil fuels, have led to the need to look for alternatives to obtain energy. The objective of this research was framed in the field of bioenergy through conventional and flash pyrolysis technologies using two agri-food waste from Asturian industries. Biomass waste is usually incinerated or accumulated, which can cause environmental problems and waste its potential as raw material to obtain biofuels and/or bio-products. The two industrial wastes used in this research were: corn cob (without grains) and a macroalgae "*Gelidium corneum*" waste generated in the Agar-agar production. Both wastes were prepared in adequate quantity and particle size to work on a laboratory scale. The pyrolysis processes (conventional pyrolysis (CP) at 750°C and flash pyrolysis (PF) at 750°C and 850°C) are based in previous works of the research group [1,2]. Each biomass waste subjected to the pyrolysis process generated three products: a solid (bio-char), a liquid (bio-oil) and a gas. These products were quantified and characterized to evaluate their possible application as biofuels or as precursors of biomaterials.

Flash pyrolysis favoured, in both cases, the formation of a more abundant gas fraction. The calorific value of the gases obtained by PF is on the order of three times higher than PC gas, mainly due to the increase in the amount of CH₄ and H₂. Bio-oils from corn cobs are suitable as biofuels. The bio-char yield obtained from macroalgae waste is close to 30% and has appreciable amounts of mineral matter. The bio-char yield from corn cobs is close to 20% and they have a high carbon content and very low mineral matter, so they would be good precursors for carbonaceous absorbent materials.

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Brownmillerite Calcium Ferrite, a Promising Perovskite- Related Material in the Degradation of a Tight Dye under Ambient Conditions

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Keywords: Brownmillerite, Nanoperovskite, Organic Pollutant, Alizarin Red-S, TD-DFT

Brownmillerite materials belong to the family of perovskite related compounds and possess the chemical formula $A_2B_2O_5$ [1]. Evaluation of effective and low-cost materials as catalysts to combat the threat of pollution is a significant and growing trend. With this aim, we have synthesized calcium ferrite brownmillerite by Pechini preparation approach as a catalyst for pollution. For such, analytical reagents $Ca(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_2 \cdot 9H_2O$, and citric acid ($C_6H_8O_7 \cdot H_2O$) were added to 20mL of distilled water in a molar ratio of 1:1:5. The structural analysis is established by the X-ray diffraction of $Ca_2Fe_2O_5$, whereas the tetrahedral and octahedral sites band stretching for ferrite specimen has been deduced using FTIR. The bandgap energy has been estimated by the Tauc relation (2.17 eV). $Ca_2Fe_2O_5$ brownmillerite exhibits a BET surface area of 10 m²/g and BJH pore volume of 0.121 cm³/g with the average particle size of 70 nm. The chemical composition of the prepared samples was confirmed using EDX and XPS analysis [2]. Importantly, the alizarin Red S dye degradation has been studied using the prepared ferrite catalyst, under dark ambient conditions and without the presence of any acidic or basic additives. Degradation is also supported by both FTIR and TOC analysis. Surface properties of brownmillerite $Ca_2Fe_2O_5$ have been characterized using electronic spectroscopy and CO₂ temperature programmed desorption (TPD) analysis and revealed that the basic surface of brownmillerite $Ca_2Fe_2O_5$ offers active sites that are suitable for degradation processes. This feature of ARS was also studied theoretically. A time-dependent density functional theory analysis was conducted in water at the CAMY-B3LYP/TZP level of theory for both ARS and ARS⁻ species. We observe a good agreement with experimental results. All results show that the preparation of brownmillerite $Ca_2Fe_2O_5$ via the Pechini method is suitable to produce fine surfaces and pores with nanosized particles.

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Carbon disulfide insertion in epoxides: synthesis of cyclic trithiocarbonates catalysed by simple chloride salts

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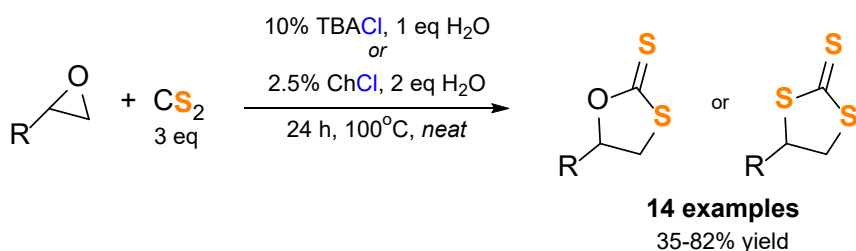
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Keywords: Trithiocarbonate, Dithiocarbonate, Carbon disulfide, Choline Chloride, Catalysis.

The insertion of heterocumulenes in epoxides is a well-known reaction as it allows the valorization of CO₂ into cyclic carbonates. In an analogous way, the use of CS₂ enables the synthesis of heterocyclic compounds with different content in sulphur (mono-, di- and trithiocarbonates) [1]. Achieving the latter requires harsh conditions [2] or metal/carbene catalysis [3,4].

Herein, we describe a procedure where this trithiocarbonates are obtained as the major products with good selectivities and yields by only using simple chloride salts (this is tetrabutyl ammonium chloride, TBACl, or choline chloride, ChCl) in low charges (2.5 – 10 mol%) and water (1-2 eq.) in neat conditions. In addition, this protocol also allows the regio-selective synthesis of dithiocarbonates (1,3-oxathiolane-2-thiones isomer).



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New insights in obtaining biofuels from tree pruning residues using different pyrolysis technologies

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Keywords: Lignocellulosic residues, Thermochemical processes, Bio-char, Biofuels, Renewable energy.

Currently, the growing demand for energy resources has led to the need to find alternative energy sources [1]. In the bioenergy field, pyrolysis processes stand out as a sustainable technology for the energy use of biomass wastes [2-3], including forest lignocellulosic residues, as will be seen in this work. The aim of this study is the energy recovery of two pruning ornamental trees residues on the Cantabrian cornice (Horse Chestnut (CI) and False Acacia (FA)). The residues were randomly collected to ensure their representativeness and were prepared to a suitable particle size for subsequent tests. A previous thermogravimetric analysis allowed the selection of the optimal variables to use in the pyrolysis processes; In this experiment, the decomposition of the lignocellulosic components (cellulose, hemicellulose and lignin) was observed. Flash pyrolysis tests (750 or 850 °C and 10 minutes of residence time) and conventional pyrolysis (750 °C and one hour of residence time) were carried out. After pyrolysis, three fractions were obtained (bio-char, bio-oil and gas), which were characterized to determine their possible final use.

The bio-chars stood out for their high carbon content and low ash content, which results in a high higher heating value (28.4-29.8 MJ/Kg), so they could be used as biofuels. The bio-oils composition differs depending on the type of pyrolysis. Those from conventional pyrolysis are mostly composed of monoaromatic hydrocarbons (~80%), where phenol (>60%) predominates, while those from flash pyrolysis are predominantly polycyclic aromatic hydrocarbons (>95%), such as anthracene or phenanthrene. The composition of the gases also varies depending on the type of pyrolysis. Conventional pyrolysis gases have a high CO₂ content (>60%), while flash pyrolysis gases have a lower CO₂ content and a higher combustible gas (CH₄, H₂) content. The high heating value of flash gases is three times higher than that of conventional gases.

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Photochemical cross-coupling of phosphorothioate salts and vinyl halides through halogen bonding-assisted generation of vinyl radicals

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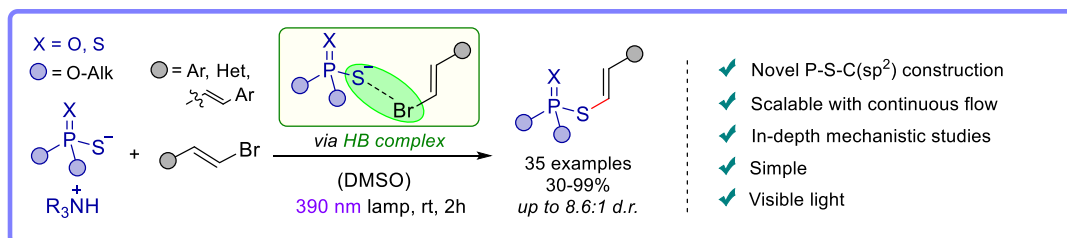
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Keywords: photochemistry • halogen-bonding • radical disconnection • cross-coupling

In recent years, there has been considerable interest in the photochemical activation of halogen-bonding complexes for the purpose of generating carbon-centred radicals under mild reaction conditions.^[1] In this field, our research group has already been successful developing a method for the generation of vinyl radicals for the construction of alkenyl sulfides.^[2]

In this work, we present a straightforward and broadly applicable synthetic procedure for the preparation of novel *S*-alkenyl and dienyl phosphoro(di)thioates through halogen bonding-assisted generation of vinyl radicals, marking the first time such compounds have been synthesized in a general way. The substrate scope is extensive, showcasing a broad tolerance for various functional groups, including some derived from natural products. Moreover, mechanistic investigations were carried out to support the existence of the halogen-bonding complex and to prove the radical-based pathway proposed. Ultimately, an efficient continuous flow protocol has been developed for the scale-up of these reactions.^[3]



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Solid-state nanochannel arrays for the diagnosis of infections caused by *Pseudomonas aeruginosa*

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Keywords: *Pseudomonas aeruginosa*, pyocyanin, infection, nanochannels, electrochemistry

Pseudomonas aeruginosa is one of the main bacterial opportunistic pathogens in patients affected with cystic fibrosis causing an increased morbidity and mortality, being also associated with nosocomial infections as urinary tract or pneumonias [1]. Clinical diagnosis and treatment of *P. aeruginosa* infections are often quite challenging due to its acquired resistance and the ease of mutation requiring the use of a broad-range of antibiotics, leading to antimicrobial resistance an emerging global healthcare problem.

Currently available methodologies employed for the identification of *P. aeruginosa* are commonly cultured-based methods, biopsy, or polymerase chain reaction (PCR), that usually require long procedures and skilled personnel that may take up to 2 or 3 days in many hospitals. However, the detection of virulence factors secreted by these pathogens has emerged as a novel potential alternative to conventional methods. Pyocyanin is an important virulence factor specific of gram-negative *P. aeruginosa*, showing crucial roles in the bacterial infection process [2].

In this context, the use of solid-state nanochannel arrays has been established as a potential tool in the biosensing field for the detection of analytes of clinical interest [3]. The sensing methodology is based on the monitoring of voltammetric signal change of a red-ox indicator, which diffusion through antibody-modified nanochannels is blocked after specific recognition of the target analyte.

Under these premises, we propose a novel sensing strategy for the detection and quantification of pyocyanin using nanochannels, without requiring the use of neither labels nor competitive assays. The zwitterion characteristics of pyocyanin will be carefully evaluated and exploited to enhance the electrostatic blockage produced inside the nanochannels after the immunorecognition event takes place.

We envisage our results may pave the way to a novel and advantageous methodology for the diagnosis of infections caused by *P. aeruginosa*.

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Sugarcane bagasse as a source of carbonaceous adsorbents by CO₂-activation

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Keywords: Sugarcane bagasse, physical activation, active carbon.

Sustainable, abundantly available and low-cost feedstocks are an attractive option in the development of carbon-based materials with adequate textural properties and chemical composition to be utilised in the removal of contaminants from air, soil, and water. The efficiency of these adsorbents depends on the precursor properties, the synthesis method, the structural modifications induced in the carbon matrix and the incorporation of functional groups. Activated carbons can be prepared through physical or chemical methods. Generally, physical activation is a two-step process involving carbonizing raw materials at a specific temperature and subsequent activation of the resulting char in suitable oxidizing gases such as CO₂, steam, and air, individually or blended.

When considering agricultural residues as renewable carbon sources, sugarcane bagasse spark interest as a potential precursor of carbonaceous adsorbents. This residual material, obtained after crushing and extracting juice from the sugarcane stalk, is rich in lignocellulosic components, with cellulose covering nearly half of the cell-wall (40–50%), and other two biopolymers, hemicellulose (25–35%) and lignin (20–25%), being responsible for the integrity of the biomass. Small amounts of other organic compounds with low to moderately high molecular weights (extractives) and inorganic minerals are also present.

This work evaluates the thermal behaviour of sugarcane bagasse using a simultaneous thermogravimetric analyzer by applying: (i) a conventional two-step physical activation process (carbonization followed by activation in CO₂), and (ii) a single-step process using CO₂, seeking lower energy consumption and shorter processing time.

In this work, the composition and CO₂-activation are compared for the two parts of the sugarcane stalk: the outside rind, more rigid and with lengthy arranged random fibres, and the inner pith, softer and with shorter fibres. Additionally, spontaneously fermented stalk and lignocellulosic components were included in the comparative study.

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Theoretical characterization of optical properties in organic systems through the partition of the first hyperpolarizability into atomic contributions

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Keywords: QTAIM, Hyperpolarizability

The purpose of this work was to propose a methodology for obtaining the atomic contributions of the majority component of static first hyperpolarizability within the framework of quantum theory of atoms in molecules. Therefore, a theoretical study was conducted on 14 donor-pi-acceptor type molecules, where the calculation of the contribution of first hyperpolarizability to the majority component was performed using the finite difference method under the framework of quantum theory of atoms in molecules. The geometries and wave functions as a function of electric fields were obtained using Gaussian 09 software with density functional theory using the ω B97X functional and a 6-311G(d,p) basis set, while the contributions of dipole moment components were obtained using Aimall software. The conclusions are as follows: a new scheme for obtaining the majority component of first hyperpolarizability was proposed, where it can be observed that the largest contributions at the individual level are from atoms present in double bonds, and at the level of functional groups, there is an increase in contribution as the strength of the donor group or acceptor group increases, thus highlighting the importance of conjugated double bonds and the characteristics of donor and acceptor groups, which is consistent with previously reported studies on such systems for the production of second-order optical phenomena, suggesting that this methodology can provide relevant chemical information that, in subsequent work, could be used for the design of new molecules with second-order optical phenomena.

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Reduction-induced $C\equiv N$ and $N\equiv O$ cleavages of acetonitrile and nitrosyl ligands at a dimolybdenum center

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Keywords: *Binuclear complexes, nitrosyl ligands, reduction reactions, N-O bond activation, acetonitrile ligands.*

Nitric oxide is a multifaceted ligand (nitrosyl) able to bind metal atoms in both high and low oxidation states and with very diverse coordination modes, which makes the chemistry of nitrosyl complexes a research area of great academic interest. Moreover, while this simple molecule has relevant biological activity at low doses (neurotransmission, regulation of blood pressure, etc.), its presence in air at high levels has undesired consequences (toxicity, greenhouse effect, ozone levels alterations, etc.) which makes it an important air pollutant requiring catalytic abatement. [1] The latter often involves the cleavage of the strong N–O bond of this molecule when interacting with one or more metal atoms at the surface of solid catalysts.

Our research group has been focusing for some time on the study of different reduction reactions as a way of obtaining unsaturated binuclear compounds that might induce activation of NO ligands at a dimetal site [2]. The reduction reaction in acetonitrile of a new system bearing P^tBu_2 as a bridging ligand, $[Mo_2Cp_2(\mu-P^tBu_2)(\mu-Cl)(NO)_2]$, resulted in two different unexpected products, stemming from two very different, but interesting processes.

When the reduction reaction was performed at 298 K, an anionic vinylidene complex was obtained, following from the $C\equiv N$ cleavage of a coordinated acetonitrile ligand, which upon protonation with NH_4PF_6 resulted in the ethylidyne complex $[Mo_2Cp_2(\mu-P^tBu_2)(\mu-CCH_3)(NO)_2]$. However, when the reaction was time-controlled and performed at 273K, the acetamidinate complex $[Mo_2Cp_2(\mu-P^tBu_2)(\mu-\kappa N:\kappa N'-NHCMenH)(\mu-NO)]PF_6$ was obtained, through a process thought to occur from a paramagnetic acetonitrile-bridged intermediate, $[Mo_2Cp_2(\mu-P^tBu_2)(\mu-NCMe)(NO)_2]$, followed by a complex series of elementary steps, these including the N–O bond cleavage of a nitrosyl ligand and reductive coupling between nitrene and iminoacyl ligands. Similar experiments are currently being carried out using different nitriles as solvents to track the elementary steps involved in the complex transformations leading to the above products.

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Platinum Quantification on Subcellular Compartments by Inductively Coupled Plasma Mass Spectrometry for evaluating Pt-drugs outcome

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Keywords: platinum quantification, nucleolus isolation, FIA-ICP-MS, cancer.

Platinum (Pt)-based chemotherapy is pivotal in cancer treatment, demonstrating high efficacy in promoting cell death by forming adducts with DNA [1]. However, recent studies have suggested an alternative mechanism of action based on the induction of nucleolar stress that finally recruits immune cells to destroy the tumor. To deepen this hypothesis, a detailed analysis of the cellular Pt distribution is required, with a special focus on the nucleolar compartment and its molecular components (i.e., DNA, RNA, protein). To this end, both an optimized protocol for the isolation of enriched nucleoli and a highly sensitive technology for the quantification of Pt are needed. Here, we have applied the flow injection analysis technique coupled with inductively coupled plasma mass spectrometry (FIA-ICP-MS) for the Pt determination of isolated nucleoli.

Specifically, two cancer cell lines (A549, lung cancer; and DU-145, prostate cancer) were treated with Pt compounds for 4h and 8h. Cell viability assays were performed to evaluate cell death induction and two gradient-based strategies (including either a single- or two-step fractionation) for the isolation of the nucleolar fraction were tested [2]. Enrichment of nucleoli was validated by Western Blot. Results reported a better performance of the two-step nucleolar isolation method and a significantly different uptake of the two tested Pt compounds (at the fg level).

Overall, this study has confirmed the applicability of the robust FIA-ICP-MS analytical tool for delivering accurate and reliable Pt quantification results, even at the subcellular level, when combined with the optimal subcellular isolation strategy.

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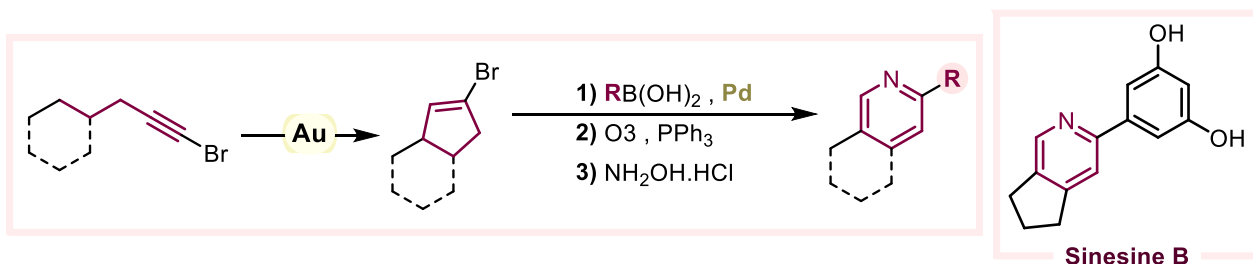
Synthesis of 2,5-Disubstituted Pyridines using the Gold(I) - Catalyzed Cycloisomerization of 1-Bromoalkynes as Key Step

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Keywords: Gold catalysis; C—H activation; bromoalkyne; condensation; application.

The gold-catalyzed cycloisomerization reaction of 1-bromoalkynes developed by Barrio and coworkers¹ has an upcoming potential. Its versatility has been proven in several cases.² Herein we show a useful application of the aforementioned reaction. The thus obtained bromocyclopentene products have been used as substrates in a 3-step synthetic sequence comprising a cross-coupling reaction, followed by ozonolysis, and final condensation towards the corresponding 2,5-disubstituted pyridines.^{2b} In addition, bicyclic fused pyridines are achieved, including the first total synthesis of the natural product Sinesine B.



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Nanoplastics obtention by mechanochemical degradation

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Keywords: nanoplastics, mechanochemistry, ball-milling, degradation.

Nanoplastics present a significant environmental challenge due to their small size and unique characteristics. They have the ability to penetrate biological barriers, thereby posing a threat to various living organisms. The study of these particles is particularly challenging since they are tiny and difficult to detect and isolate within aquatic environments. Currently, new methods are under development to obtain nanoplastics in order to simulate synthetic waters and establish a standardized protocol for their study.

A promising alternative for obtaining nanoplastics involves the use of ball mills to physically break down larger plastics. This approach is based on the principles of mechanochemistry, which is an environmentally friendly method increasingly utilized in various fields such as materials science, polymer chemistry, and organic and inorganic synthesis.

In this research, a mixer-type ball mill, featuring an oscillatory horizontal motion, was employed to degrade five of the most widely used plastics globally: PET, PP, PVC, HDPE, and LDPE. The advantage of this method is that it does not require additional solvents, reducing costs, and the milling time was optimized for each specific plastic type. Sample characterization was conducted using electron microscopy and laser diffraction. The average particle size obtained was 10 nm for all plastics, except for PVC, where a size of 270 nm was achieved.

This advancement represents a significant step forward in the study of nanoplastic removal from water. It offers a valid method applicable to various plastic types and enables the attainment of smaller particle sizes compared to those achievable using other technologies.

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Correction of creatine-creatinine conversion during serum creatinine quantification by two-dimensional liquid chromatography and double-spike isotope dilution tandem mass spectrometry

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Keywords: serum creatinine, bidimensional chromatography, tandem mass spectrometry, double spike isotope dilution, analyte interconversion

Development of a candidate reference method based on bidimensional liquid chromatography coupled to ESI-MS/MS and double spike isotope dilution for serum creatinine quantification capable of correcting for creatinine-creatine interconversion during sample pretreatment. Study of the impact of the creatine-creatinine interconversion during the analysis of human serum samples. $^{13}\text{C}_1$ -creatinine and $^{13}\text{C}_2$ -creatine are added to the serum sample. Separation carried out by bidimensional liquid chromatography combining reversed phase and a strong cation exchange chromatography. The heart cut, containing creatine and creatinine, is automatically transferred to the second dimension. Quantification carried out by double spike isotope dilution tandem MS/MS.

Results: Minimization of spectral interferences and ion suppression due to matrix effects while increasing sample throughput compared to the direct coupling of cation exchange chromatography to the ESI source. Trueness of the method studied with the satisfactory analysis of two certified reference materials. Satisfactory intra- and inter-day precisions obtained analysing a serum pool and control sera. Analysis of 93 serum samples revealed negligible interconversions with no correlation with creatine levels.

Conclusions: The method provides adequate analytical figures of merit for serum creatinine determination according to CSLI guidelines. Negligible creatine-creatinine interconversion is promoted with the applied sample preparation procedure.

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Floating electrochemical platform based on pencil leads for the determination of venlafaxine in inland waters.

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Keywords: emerging contaminants, antidepressant drug, electroanalysis, pencil leads electrodes.

Water is an essential commodity, but its availability is increasingly scarce due to natural deterioration, industrialisation, overpopulation and climate change. Studies carried out to assess water quality focus on priority pollutants such as heavy metals, additives and microbiological analyses. However, recent works reveal the presence of a multitude of organic compounds (e.g. pharmaceuticals) that significantly affect water quality, even in low concentrations. These emerging contaminants (ECs) are difficult to remove with conventional treatment processes in wastewater treatment plants (WWTPs), and thus a large part of them can be discharged into effluents, which cause health risks to aquatic species and humans.

The determination of the ECs is an important challenge due to their variability in terms of physical and chemical properties, and their spatial-temporal variations in their distribution caused by seasonality, inter- and intra-day variations and/or occasional events. Thus, decentralized equipment, that can be easily deployed in water sources for performing simple methodologies, must be rapidly developed.

With this aim, we have already developed a small and very low-cost paper-based electroanalytical device for the determination of an anti-inflammatory drug [1]. In this work, the challenge extends to floating electroanalytical platform based on pencil leads as electrodes combined with a tiny potentiostat for in-situ analysis of venlafaxine (antidepressant drug) in inland waters. The composition of the pencil leads and area electroactive used, as well as experimental parameters, have been thoroughly assessed to achieve optimal electroanalytical features. This simple methodology shows a good analytical performance with great accuracy in measurements despite being handmade with low-cost materials.

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Black Liquor Acidification and Adsorptive Separation of Organic Acids

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Keywords: Black liquor, acidification, wet oxidation, adsorption, organic acids.

The global production of cellulose pulp, primarily through the Kraft method, generates massive amounts of black liquor. Its conventional treatment, involving evaporation and combustion, though profitable, involves operational and environmental drawbacks, resulting in the loss of high-value compounds. Lignin separation by acid precipitation is an alternative already implemented industrially. However, this method leaves an aqueous solution with untapped compounds [1]. Adsorption is studied here as an effective method to separate and purify these compounds.

A previous wet oxidation treatment (190 °C, 70 bar, 210 min) was found to enhance the purity of the delignified fraction [2], making it viable for organic acids extraction. Oxalic, acetic and lactic acid were detected as the main components of this delignified and oxidized fraction. Adsorption under basic conditions may exhibit lower efficiency due to the deprotonation of the organic acids. The designated oxidized phases are adjusted to pH 1.2 to investigate the impact of acidity on the process.

The recovery of these acids by adsorption was tested using two granulated activated carbons (GAC), FILTRASORB® 300 and NORIT® GAC 830, by employing various solid-liquid ratios to establish an optimal model and investigate isotherms. Results revealed that those more acidic samples exhibited a higher adsorption of the organic acids, corroborating that this behavior is directly related to their corresponding pKa values. Simultaneously, the reduction in color number observed, proportional to the amount of GAC, implies that remnants of lignin or other phenolic compounds are adsorbed along with the acids. Despite this, salts were not significantly adsorbed, allowing a successful purification of the organic compounds.

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Acid Catalyzed Generation of Alkenyl Cations and their Participation in *gem*-Diarylation Reactions and Related Processes

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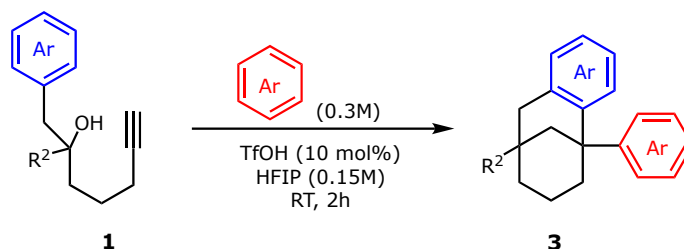
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Keywords: cationic cyclization, diarylation reaction

Carbocations are of exceptional significance being crucial reactive intermediates in synthetic processes and playing an important role in elucidating the mechanisms behind a wide array of (bio)chemical transformations. We and others have studied a method for the generation of cyclic alkenyl cations through the cationic cyclization of systems containing an alkyne as terminating group. We have also studied the subsequent capture of this intermediate with different heteroatomic nucleophiles.^[1]

In this context, we studied the capture of alkenyl cations, generated through a cationic cyclization process, with simple arenes (**1**). Previous reports suggested that a simple arylation process to give an aryl-substituted alkene should be observed.^[2] However, when the reaction was performed in 1,1,1,3,3,3-hexafluoropropan-2-ol using 10 mol% of triflic acid as catalyst, we isolated the benzofused bicyclic product **3** in quantitative yield. Herein, we present our studies of this novel *gem*-diarylation reaction.



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Stroke differential diagnosis in nasal exudate and serum using elemental analysis, HPLC post-column isotopic dilution ICP-MS and targeted protein determination

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Keywords: Stroke, nasal exudate, serum, HPLC-ICP-MS, Fe binding protein

Stroke occurs when the blood flow in the brain decreases, either due to a broken vessel (hemorrhagic) or because of a blood clot (ischemic). It is considered the second cause of death worldwide, and there is also a high morbidity associated with this pathology. As the brain is highly immunoprotected, the access to direct clinical parameters associated with stroke is rather limited. In fact, diagnosis is basically done by means of imaging techniques at hospitals and there are currently no clinical biomarkers that can distinguish between a hemorrhagic or an ischemic stroke. 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 stroke [1]. Fe is an essential element in the human body, and it plays an important role in neurotransmission and oxygen transport processes. Brain cells maintain Fe homeostasis by regulating Fe import, storage, metabolism, and export, so Fe binding proteins take part in the regulation of brain Fe. In this context and aiming at the search of potential biomarkers for differential diagnosis of stroke, differences in Fe levels (free Fe, Fe protein profile and total Fe) have been investigated for three different cohorts: hemorrhagic stroke, ischemic stroke, and a control group. For such purpose, a method based on SEC-HPLC, coupled to ICP-MS and quantitative analysis via post-column isotope dilution (IDA) has been developed, also elemental analysis and protein levels of Fe-binding proteins (ferritin, ferroportin and transferrin) have been considered. Apart from nasal exudate parallel studies using serum, have been also performed as it is the most common fluid used for diagnosis.

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Chemical – nutritional characterisation of *Moringa oleifera* to prevent infant undernutrition in Mali

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Keywords: Bromatology, undernutrition, *Moringa oleifera*, dietary supplement.

Due to the increasing prevalence of undernutrition in young children in Mali, Africa, there is an urgent need to develop complementary strategies to prevent this condition. An effective model involves the use of local food in order to improve nutritional quality and promote the sustainability of food production [1], with low-cost, available, accessible and culturally coherent ingredients. *Moringa oleifera* is a versatile tree, capable of growing throughout the tropics and subtropics, noted for having abundant applications in traditional medicine and nutritional compounds with the potential to play a role in the diversification and contribution of the diet to alleviate hunger in Mali [2 – 3].

This study focuses on the chemical-nutritional characterization of *Moringa oleifera*, exploring its viability as a dietary supplement for children in Mali. The research addresses the composition of Moringa leaves and seeds, using gravimetric, spectrophotometric and chromatographic techniques. Alternatively, the contribution of Moringa towards the daily nutrient requirements was evaluated, as well as its impact on anthropometrics and blood parameters in children from 0 to 2 years old. The results revealed significant concentrations of proteins (27.3 g), calcium (1400 mg) and potassium (1100 mg) in the leaf powder, while the seeds presented a high protein (32.5 g) and oil content (42.8 g) expressed per 100 g of dry matter. It was observed that 20 grams of Moringa leaf powder is capable of satisfying the calcium requirements and half of the protein requirements in the initial stages of development, although no significant differences were observed in the blood analysis due to the lack of follow-up of the study.

It is concluded that *Moringa oleifera* is a nutrient dense food, with the potential to address childhood undernutrition in Mali. However, further research is required in order to determine the consequences of its administration during this essential stage of development in children.

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Evaluation of different fatty acid derivatization procedures suitable for the development of an Isotope Dilution Mass Spectrometry quantification method

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Keywords: mass spectrometry, fatty acid, derivatization, isotopic dilution.

Polyunsaturated fatty acids (PUFAs), mainly omega-3 and omega-6, are essential fats that must be obtained from the diet. These compounds are involved in certain biological processes, such as inflammation or neurotransmission regulation. Many studies highlight the potential benefits of including omega-3 rich foods in the diet and the importance of keeping well-balanced levels of omega-3 and omega-6 to maintain a good health condition. Their potential relationship with multiple diseases such as diabetes, cardiovascular diseases and even cancer, has been suggested, but despite their role as potential biomarkers is still unclear, there is an increasing interest in the development of robust and accurate methods for their reliable determination. In this context, the development of isotope dilution and mass spectrometry (IDMS) quantification methods is convenient, as it ensures the comparability of the results when analysing different biological samples. The development of IDMS methods for determination of biomolecules usually requires a chromatographic separation prior to the MS detection due to the complexity of the biological matrices. FAs are typically separated by GC, although HPLC separation methods are also found in the literature. However, regardless of the chromatographic technique used for their separation, the derivatization of FAs is always required, as due to their low volatility, low ionization efficiency and presence of matrix effects the GC or HPLC separation and/or the MS detection might be hampered. In this work, several derivatization reagents are tested. The optimization of the chromatographic separation conditions for the separation of the derivatized analytes by for both, GC and HPLC, are presented. The suitability of the different tested derivatization reagents is evaluated in terms of selectivity and sensitivity. The isotopic distribution of the compounds of interest after EI ionization is also studied, to account for the possible in-source loss of the isotope labels, hampering the development of the IDMS quantification method.

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Extraction of carotenoids from egg yolk using sunflower oil as green solvent

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Keywords: carotenoids, egg yolk, green solvents, sunflower oil

Carotenoids constitute a group of organic chemical compounds naturally found in the chromoplasts and chloroplasts of plants, photosynthetic algae, fungi and bacteria [1]. Classified into carotenes and xanthophylls, these natural pigments exhibit a wide range of bioactive properties, making them interesting additives in the food, cosmetic and nutraceutical industries as natural colorants, antimicrobials, and antioxidants [2]. In this sense, the extraction and purification of carotenoids is a field of study that has gained significant importance in recent years, particularly the study of the use of green solvents or environmentally friendly techniques. Therefore, the aim of this study was to optimize the extraction of carotenoids from egg yolk using sunflower oil as solvent, and to explore the potential application of these extracts as colorants in the food and nutraceuticals industries.

For this purpose, extractions were carried out by varying parameters like reaction time, temperature, and homogenisation speed. In addition, extractions were performed from the entire egg yolk and from its individual components, plasma and granules, to study the interactions between the sunflower oil and the different carotenoids and lipids present in each fraction. Carotenoid concentration in each extract was measured to determine the optimum extraction conditions. Subsequently, the colour parameters and photostability of the best extract were analysed. Sunflower oil extracts enriched with carotenoids exhibited a clearly orange coloration, which proved its possible use as natural colorant. Moreover, this enriched oil showed a greater stability against photooxidation than normal sunflower oil, which evidences the antioxidant effect of the carotenoids present in it.

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Comparison of different internal standardization approaches for untargeted metabolomics analyses by GC-QTOF

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Keywords: High-resolution mass spectrometry, gas chromatography, derivatization

Serum is a widely used matrix in metabolomics for the discovery of novel candidate biomarkers. It contains a large variety of metabolites (molecules smaller than 1500 Da) in a higher concentration than in plasma [1]. The use of high-resolution mass spectrometry (HR-MS) in combination with a chromatographic separation technique allows the detection and separation of thousands of metabolites in a single analysis.

The vast majority of serum metabolites are not detected by gas chromatographic (GC)-HRMS analysis as they are not volatile. Thus, derivatization is required to make them volatile and thermally stable prior analysis. Silanisation using derivatization reagents such as BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) or MTBSTFA (N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide) are widely used for metabolomic studies [2]. Both reagents provide several advantages and disadvantages. For example, BSTFA allows the derivatization of sugars, but MTBSTFA provides better yields when derivatizing small molecules such as amino acids. We propose here a sequential derivatization approach involving both reagents and different standardization approaches based on the use of several internal standards that will be tested in real serum samples and Quality Controls (QCs).

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Study of the effect of different fatty acids as main carbon source in the biosynthesis of bioplastics (PHAs)

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Keywords: fatty acids, polyhydroxyalkanoates, waste vegetable oil

The depletion of fossil resources and rising environmental concerns led to a surge in the exploration of bio-based plastics [1]. Among these, polyhydroxyalkanoates (PHAs), recognized as microbial polymers, have risen as a sustainable alternative to petrochemical plastics, distinguished by their hydrophobicity, thermoplasticity, and inherent biodegradability. Among bacterial strains, *Cupriavidus necator* stands out as one of the most studied and productive when it comes to producing polyhydroxyalkanoates (PHAs). These microbial polymers serve as an energy reservoir, accumulating when essential elements like nitrogen and phosphorus are limited, while carbon is plentiful. Notably, vegetable oils have demonstrated exceptional efficacy as carbon sources for PHA production, yielding 0.6-0.8 g of PHA per gram of oil. While waste cooking oil stands out as a potential source for these polymers, its variable composition raises uncertainties regarding the impact of individual fatty acids on PHA production yield and monomeric composition. To address this, our study systematically evaluated how prevalent fatty acids in waste vegetable oils influence both PHA production and polymer characteristics. The experiments involved varying concentrations of each fatty acid (5 and 15 g/L) and were monitored over a week (168 hours). Results revealed a notable preference for unsaturated fatty acids (PUFA) over their saturated counterparts. Particularly, utilizing oleic acid (C18:1) as the sole carbon source at 15 g/L for 144 hours led to the highest PHA production yield at 6.7 ± 0.7 g/L. Importantly, the type of fatty acid did not influence the fundamental monomeric composition of PHAs, all of which comprised hydroxybutyrate (HB) monomers. In conclusion, waste cooking oils enriched with oleic acid, such as waste olive oil, emerge as promising substrates for PHA production, anticipated to yield polymers with commendable mechanical properties. This study has the potential to enhance the feasibility of utilizing various fatty waste streams for PHA production [2,3].

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Catalyst-Free Regioselective 1,2-Diheterofunctionalization of Vinylferrocene

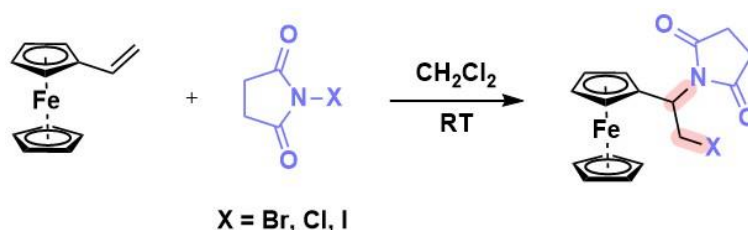
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Keywords: addition reactions, diheterofunctionalization, N-halosuccinimides, multicomponent reactions, vinylferrocene

Functionalized ferrocenes have widespread applications in catalysis, materials science, and medicinal chemistry, prompting ongoing research into efficient synthesis methods from readily available materials. Vinylferrocene is a versatile building block, but despite nearly seven decades of intensive exploration into its reactivity, the incorporation of two different heteroatom motifs across its olefinic backbone remains an underexplored yet highly desirable pursuit. In this study, we report a catalyst-free aminohalogenation process applied to vinylferrocene, employing *N*-halosuccinimides (NXS; X = Cl, Br, I) as dual nitrogen and halogen sources. This 1,2-diheterofunctionalization reaction takes place with complete regioselectivity, wherein the terminal carbon atom of the vinyl group selectively reacts with the electrophilic halogenating reagent, resulting in the formation of a cationic intermediate, which is subsequently captured by the succinimide anion. The structure of the key cationic intermediate was studied using theoretical methods. This intermediate can react with alternative nucleophiles, enabling a three-component strategy for the synthesis of novel 1,2-diheterofunctionalized ferrocene derivatives.^[1]



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C-H activation of Unbiased C(sp³)-H Bonds: Gold(I)-Catalyzed Cycloisomerization of 1-Bromoalkynes

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Here, we present a gold(I)-catalyzed C(sp³)-H functionalization of 1-bromoalkynes without any sort of electronic, or conformational bias.^{1,2} Moreover, it doesn't need any directing group.³ The reaction proceeds regioselectively and stereoselectively to the corresponding bromocyclopentene derivatives. The latter can be readily modified, comprising an excellent library of diverse 3D scaffolds with very high C(sp³) fraction (F_{sp³}) for medicinal chemistry.⁴ In addition, a mechanistic study has shown that the reaction proceeds via a so far unknown mechanism: a concerted [1,5]-H shift / C-C bond formation involving a gold-stabilized vinylcation-like transition state⁵.

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Validated Routine Procedure for the Determination of Butylated Organotin Compounds in Sediments by Isotope Dilution Gas Chromatography Coupled to Triple Quadrupole Mass Spectrometry

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Keywords: TBT, GC-MSMS, IDMS, sediments, routine

The use of organotin compounds, especially TBT, on ships as anti-fouling agent was banned in 1999 by the International Maritime Organization (IMO) due to their risk for the marine environment. Unfortunately, butylated organotin compounds have remained in the environment due to their high stability, accumulating in marine sediments [1]. Current European legislation requires the continuous monitoring of the levels of organotin compounds in coastal marine sediments. Therefore, the aim of this work was to develop a fast and reliable analytical methodology to routinely quantify the levels of TBT, DBT and MBT in marine sediments at the low ng/g levels (dry weight). The technique chosen was Gas Chromatography coupled to tandem Mass Spectrometry after ethylation of the organotin compounds. Extraction of the organotin compounds from the sediment was carried out by a mixture of methanol and acetic acid (1:3 by volume). Quantification was carried out by Isotope Dilution Mass Spectrometry (IDMS) using ¹¹⁹Sn-labelled compounds [2]. The detection limits achieved for TBT, DBT and MBT were 0.3, 0.3 and 0.1 ng·g⁻¹ respectively. Validation was carried out with three reference materials (BCR-462, BCR-646 and PACS-2) with satisfactory results. Relative standard deviations were, in all cases, less than 5% for all compounds. Finally, 97 real marine sediment samples were measured.

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Marriage between chiral [2.2]paracyclophanes and BODIPYs. A new family of small organic emitters of CP light

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Keywords: Organic dyes, BODIPY, [2,2]Paracyclophane, chirality, CPL

Efficient emitters of circularly polarized light (CPL) based on simple organic molecules (SOM) are highly sought after for the development of advanced photonic materials and applications, such as CP-OLEDs, CP-bioprobes, or dye CP-lasers [1]. BODIPYs constitute a well-known family of organic dyes that have found use in a wide variety of photonic applications due to their structural versatility and excellent photophysical properties, particularly fluorescence [2]. However, the BODIPY chromophore is inherently planar, lacking the chirality necessary to serve as an emitter of CP light. Strategies developed to date to achieve CPL-enabling BODIPYs include attaching suitable chiral moieties to the BODIPY core or embedding it in a chiral molecular architecture [1]. However, the level of circular polarization achieved for the best CPL-active BODIPYs developed to date is still low [4], and new chiral designs are urgently needed to advance these interesting CPL-SOM emitters. In this context, chiral [2.2]paracyclophanes (PCPs) represent an interesting chiral scaffold for this purpose, owing to the unique small three-dimensional structure of the PCP system [5]. We became interested in exploring this possibility by chemically joining fluorescent BODIPYs dyes and chiral PCP systems using palladium-catalyzed C-C coupling reactions. Herein, we describe preliminary synthetic results from this investigation.

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Extending the thermo-oxidative stability of EVOO supplemented with polyphenols under deep-frying

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Extra virgin olive oil (EVOO) is an excellent nutrient source amongst the edible oils thanks to its monounsaturated fats, natural antioxidants, and unique organoleptic properties [1]. Deep-frying produces objectionable flavors and changes the quality and stability of EVOO by hydrolysis, oxidation, and polymerization followed by oil degradation, that affect the safety, health, and shelf-life of EVOO and fried food negatively [2-3]. Nevertheless, the oxidative deterioration of frying EVOO was little protected by endogenous antioxidants, including carotenoids and tocopherols, as well by synthetic antioxidants. In this study, an experimental design methodology at lab-scale was conducted to carry out optimization of deep-frying experiments throughout different conditions (olive oil variety, temperature, time, and polyphenols supplementations). The evaluations performed were physicochemical properties including: acidity, indices of peroxides, specific extinction coefficients (UV absorption). The sensorial characteristics of the EVOO samples were also assessed by a panel. The results show that a gradually decrease in the physicochemical quality indices and oxidative stability were observed when the temperature and time of the frying are increased (from 170 to 210 °C for 3 and 6 h). Changes in the evaluated parameters were found as a function of the heating time and temperature. Furthermore, EVOO supplemented with polyphenols was found to be more stable under deep-frying, these natural constituents offer good protection of EVOO against oxidative deterioration without decreasing the positive sensory attributes of EVOOs e.g., fruity, bitter and pungent properties. This research provides a comprehensive understanding of the effect of polyphenolic compounds on the stabilization of EVOO and their working mechanisms against thermo-oxidation under deep-frying conditions. These findings will provide the potential insights on the possible application of natural antioxidants as the stabilizers of frying EVOO in food industry. In conclusion, the current study confirmed that polyphenol substances are applied in EVOO, the oxidation stability is significantly improved.

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Synthesis and characterization of different Isotopically Enriched Inorganic Nanoparticles for Biological Applications

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The development of new bioanalytical methodologies capable of assessing the presence, distribution, transformation and elimination of inorganic nanoparticles, both in animal and plants, is required nowadays [1]. These (bio)nanoanalytical characterization strategies should be compatible with biological media [2]. Furthermore, it is desirable to be able to discriminate the natural metals present in the biological system from those present in the target nanoparticles added to be able to perform stability and distribution studies in the biological matrix more efficiently and accurately.

To meet these requirements, different nanomaterials, such as Fe-doped carbon dots and Fe nanoparticles, both isotopically labelled with ^{57}Fe , have been synthesized during this work.

The characterization and detection of these isotopically labelled nanomaterials in biological samples was performed using an instrumental platform consisting of a separation system coupled to two molecular detectors and an elemental/isotopic detector, AF4-UV/vis-MALS-ICP-MS/MS. [3] to obtain a confirmation of their presence by elemental/isotopic detection based on Mass Spectrometry measurements. Complementary analytical techniques such as UV-visible Spectroscopy, Fluorescence Spectroscopy, Multiangle Light Scattering (MALS), Dispersion Light Scattering (DLS) and Transmission Electron Microscopy (TEM) were used for the molecular characterization of the original nanoparticles.

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