CQE Days

May 25th and 26th

ABSTRACTS BOOK

PLENARY, KEYNOTE, ORAL & POSTER

Book of Abstracts of the CQE Days 2023
25th – 26th May 2023, Lisbon – Portugal
Edited by Maria João Ferreira, Gonçalo Justino, Ana Marta Matos, Ana Mestre, Nuno Neng, Pedro Pinheiro, Karina Shimizu and Maria Amália Soares

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Welcome to the 5th edition of CQE Days!

In 2019 CQE Days went live at Academia das Ciências de Lisboa. The following two editions were online due to the pandemic restrictions, and in 2022 CQE Days returned to a presential format at Faculdade de Ciências.

This year we are going back to the original venue, Academia das Ciências de Lisboa. As the CQE Days aim to share the research of all CQE members, this year all keynote lectures and all oral communications are from CQE members. We are also pleased to announce that we have a Plenary Lesson that will be given by Prof. Jorge Calado, one of the founding members of CQE..

Trying to supplant previous editions, this year we also bring you a few workshops. For the younger members we have sessions to help their development of communication and other soft skills; for more senior members, we have sessions directed at explaining/improving applications in European calls.

In this year's gathering we have circa 300 participants and about 200 communications, distributed by the four thematic lines (SYNCat, MATSoft, SUSChem, and MEDLife) that showcase CQE's contribution and commitment to research and the advancement of the field of chemistry. We hope this year's CQE Days will kindle interactions between group members and promote more than ever the establishment of stronger internal synergies between the four thematic lines.

Lisbon, May 25, 2023

The Organising Committee

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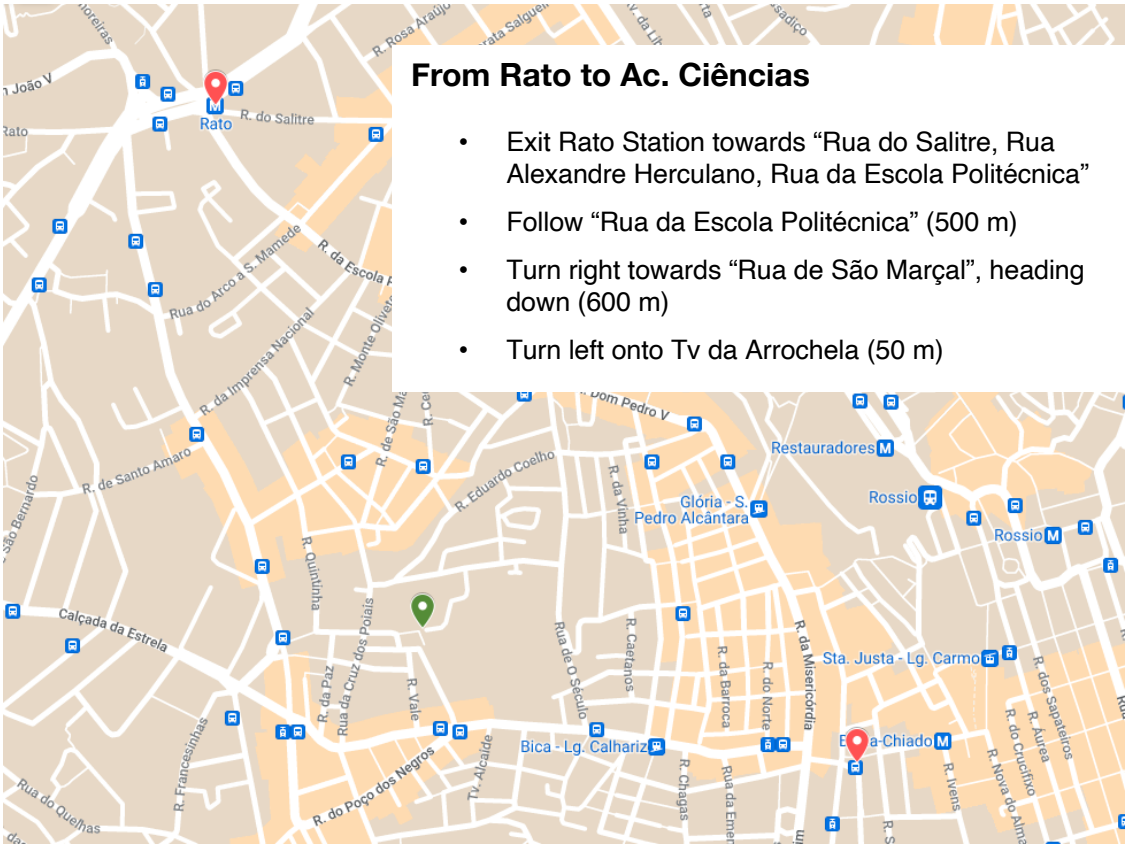

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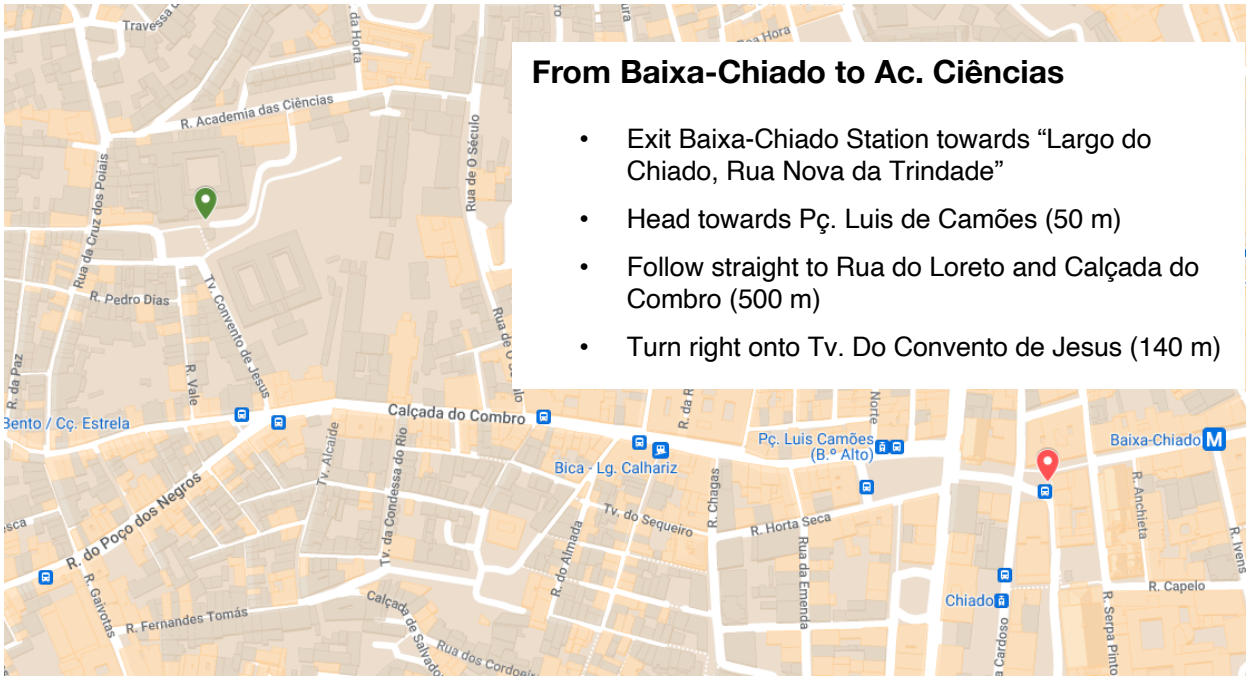
- Exit Rato Station towards “Rua do Salitre, Rua Alexandre Herculano, Rua da Escola Politécnica”
- Follow “Rua da Escola Politécnica” (500 m)
- Turn right towards “Rua de São Marçal”, heading down (600 m)
- Turn left onto Tv da Arrochela (50 m)



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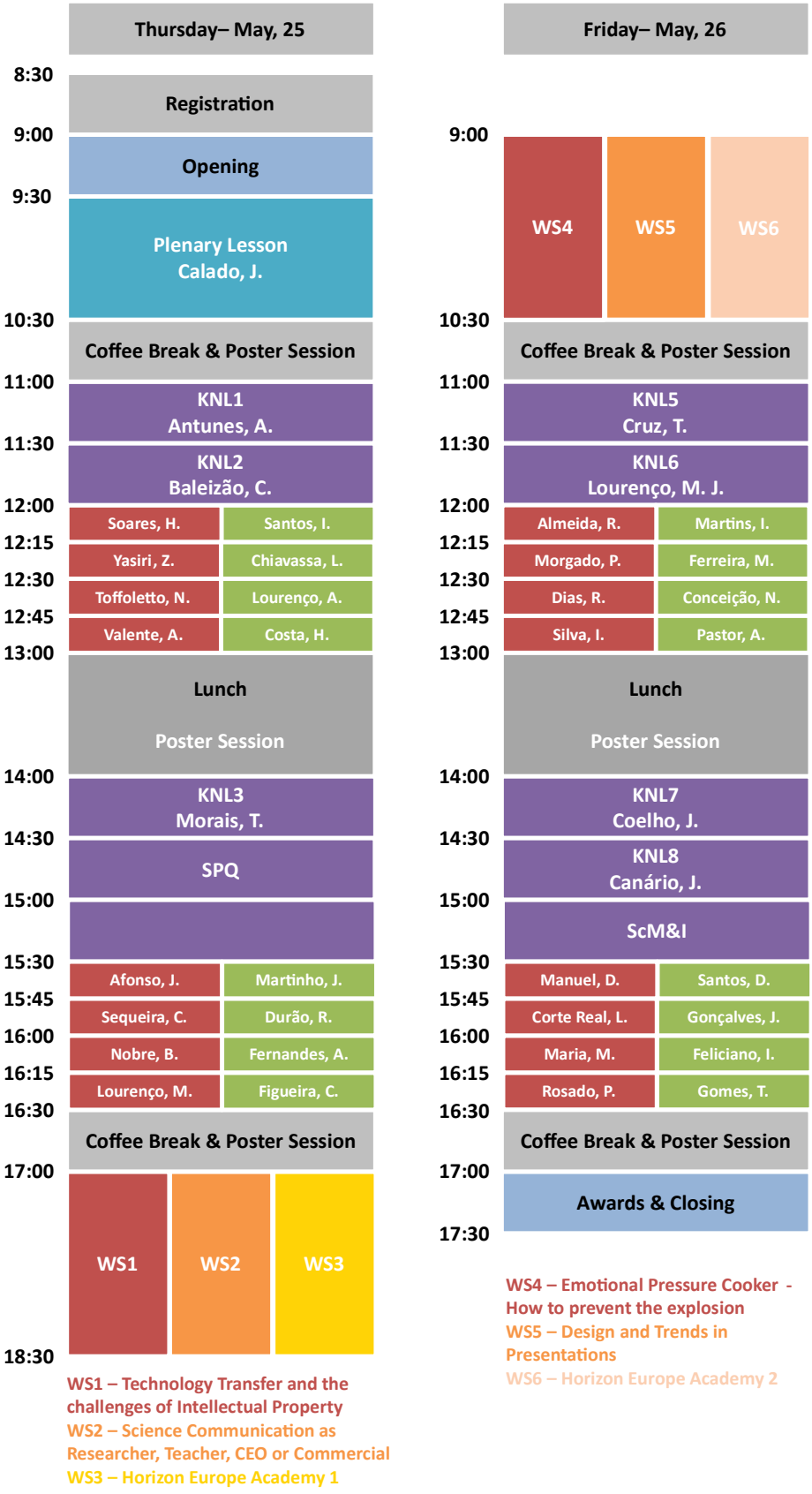
- Head towards Pç. Luis de Camões (50 m)
- Follow straight to Rua do Loreto and Calçada do Combro (500 m)
- Turn right onto Tv. Do Convento de Jesus (140 m)

Overall Programme – Presentations



Oral Presentations

Thursday Morning – May, 25

9:00 – Opening Ceremony (Salão Nobre, JN Canongia Lopes)

9:30 – Plenary Lesson: PL1 Calado (Salão Nobre, chair: G Justino)

On Being a Scientist
Jorge Calado — PL1

10:30

Keynote Session 1 (Salão Nobre, chair: G Justino)

11:00

Chemical Toxicology: from the minimization of chemically induced adverse effects to the development of diagnostic tools
Alexandra Antunes — KNL1

11:30

Smart hybrid polymer@silica nanocarriers for control release
Carlos Baleizão — KNL2

12:00

Parallel Sessions

Oral Session 1 (Salão Nobre, chair: G Justino)

12:00

Cell adhesion and associated functions are dependent on a strict regulation of TBCCD1 levels
Helena Soares — O1

12:15

Repurposing montelukast for Alzheimer's – a proteomics assessment of a new in vitro neuron model
Zainab Al-Yasiri — O2

12:30

Peptide-eluting contact lenses enhance topical drug delivery across the ocular barriers
Nadia Toffoletto — O3

12:45

A new ruthenium-cyclopentadienyl compound as a promising cancer MDR reversing agent
Andreia Valente — O4

13:00

Oral Session 2 (Aula Maynense, chair: V André, MJ Ferreira)

12:00

Stimuli responsive surfactants: towards smart templates for mesoporous silica nanoparticles
Inês Santos — O5

12:15

Smart self-healing polymer materials for supercapacitors
Luisa Chiavassa — O6

12:30

CO_2 mineralization using industrial solid wastes
António Lourenço — O7

12:45

Assessment of biomass-derived GACs for point-of-use water filters
Henrique Costa — O8

13:00

Thursday Afternoon – May, 25

	Keynote Session 2	(Salão Nobre, chair: A Mestre, C Bacariza)
14:00	**Novel approaches to fight metastatic cancer: the journey from small molecules to smart metallodrugs** Tânia Morais	KNL3
14:30	**SPQ** João Paulo Leal	
15:00		
	Parallel Sessions	
	Oral Session 3	(Salão Nobre, chair: A Mestre, C Bacariza)
15:30	**Fatty acids-based Eutectic Solvents Liquid Membranes for Removal of Micropollutants from Water** João Afonso	O9
15:45	**On Capillary Viscosity Measurements: How Far do Surface Tension Effects go?** Carolina Sequeira	O10
16:00	**Pressurized liquids to obtain DHA enrich extracts from microalga *Crypthecodinium cohnii*** Beatriz Nobre	O11
16:15	**Validation of physical-chemical tests of solid biofuels for the international accreditation of analytical capabilities** Marta Lourenço	O12
16:30		
	Oral Session 4	(Aula Maynense, chair: MJ Ferreira, T Cruz)
15:30	**Nanofibers of $LnInO_3$ perovskites (Ln= La, Pr, Sm, Dy and Yb) as catalysts for the Oxidative Coupling of Methane** Joana Martinho	O13
15:45	**Electrochemical Functionalization of Quinolizidine Alkaloid** Raquel Durão	O14
16:00	**Thermo- and Photo-responsive Spin Labile Fe(III) complexes** André Fernandes	O15
16:15	**Methyl- and phenylnickel complexes with triazole-tethered phenoxyimine ligands for the catalytic hydrosilylation of olefins** Cláudia Figueira	O16
16:30		

Thursday Afternoon – May, 25

Parallel Sessions

	Workshop 1	(Salão Nobre)
17:00	**Technology Transfer and the challenges of Intellectual Property** Patrícia Lima and Carla Patrocínio	WS1
18:30		
	Workshop 2	(Salão das Reuniões Internacionais)
17:00	**Science Communication as Researcher, Teacher, CEO or Commercial** Alexandra Antunes, Zita Martins and Tiago Silva	WS2
18:30		
	Workshop 3	(Aula Maynense)
17:00	**Horizon Europe Academy 1** Ana Espada and Patrícia Guerreiro	WS3
18:30		

Friday Morning – May, 26

Parallel Sessions

9:00	Workshop 4	(Salão Nobre)
10:30	**Emotional Pressure Cooker – How to prevent the explosion** Sofia Knittel	WS4
9:00	Workshop 5	(Salão das Reuniões Internacionais)
10:30	**Design and Trends in Presentations** Marta Daniela Santos and Patrícia Guerreiro	WS5
9:00	Workshop 6	(Sala das Sessões)
10:30	**Horizon Europe Academy 2** Ana Espada and Patrícia Guerreiro	WS6

Friday Morning – May, 26

	Keynote Session 3	(Salão Nobre, chair: K Shimizu, M Andrade)
11:00	**Exploring the potential of late transition metal complexes toward olefin, carbonyl, and carbon dioxide reduction** Tiago Cruz	KNL5
11:30	**Marine resources: discoveries and alternatives with future in Technological Chemistry** Maria José Lourenço	KNL6
12:00		
	Parallel Sessions	
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12:00	**Understanding the Thermal Conductivity of Ionic Liquids: A Direction to Select New Heat Transfer Fluids** Rafael Almeida	O17
12:15	**Perfluorinated (PFAS) Pollutants – Molecular Modelling and Simulation for Environmental Remediation** Pedro Morgado	O18
12:30	**Sustainability analysis and decision making of a Ca - Looping plant using water as fluidisation fluid for calcination** Ricardo Dias	O19
12:45	**Sodium Salt with Fatty Acids Eutectic mixtures as Electrolytes for Supercapacitors** Inês Silva	O20
13:00		
	Oral Session 6	(Aula Maynense, chair: S Realista, N Xavier)
12:00	**Continuous-Flow Electrochemical Oxidation of Abietanes** Inês Martins	O21
12:15	**The unexpected reactivity of Ruthenium hydrides supported by di -tert-butylpyridylphosphine** Maria João Ferreira	O22
12:30	**Peroxidative oxidation of cyclohexane in aqueous CH_3CN medium using Cu(II or I) complexes bearing hydrazone or 1,3,5 -triaza-7-phosphaadamantane-derived ligands** Nuno Conceição	O23
12:45	**Study of new Ni-based coordination polymers as promising De -NOx photocatalysts** Adrián Pastor	O24
13:00		

Friday Afternoon – May, 26

Keynote Session 4 (Salão Nobre, chair: P Pinheiro, G Justino)

14:00 – 14:30
Data-Driven Prediction of Bioorthogonal Reactions
Jaime Coelho — KNL7

14:30 – 15:00
Climate change in the Arctic: Chemistry as a crucial tool to measure, understand and mitigate
João Canário — KNL8

15:00 – 15:30
ScM&I
Ana Espada and Patrícia Guerreiro

Parallel Sessions

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15:30 – 15:45
Synthesis of novel D-glucopyranuronamide-based nucleoside analogs of potential anticancer interest
Domingos Manuel — O25

15:45 – 16:00
Exploring the anticancer potential of novel Cu(II) and Zn(II) complexes of 8-hydroxyquinoline Schiff bases
Leonor Corte-Real — O26

16:00 – 16:15
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Marisa Maria — O27

16:15 – 16:30
Targeting PBP2a to overcome β-lactam resistance in methicillin-resistant *Staphylococcus aureus*
Pedro Rosado — O28

Oral Session 8 (Aula Maynense, chair: A Mestre, V Ferreira)

15:30 – 15:45
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Daniel Santos — O29

15:45 – 16:00
Stimuli-Triggered Activated Nanoparticles to Eliminate Formaldehyde Emission
José Gonçalves — O30

16:00 – 16:15
Thermodynamic and Kinetic approach of the Formation of Multicomponent -Crystals with Different Stoichiometries: Maleic Acid and Phenylalanine
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16:15 – 16:30
Studying shifts in the magnetic behaviour of iron complexes via ligand and counterion modifications
Tiago Gomes — O32

17:00 – 17:30
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CQE | Infrastructure & Facilities

Thursday and Friday Coffee Break and Lunchtime – May, 25 and 26

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biobank|CQE: a powerful tool for medicinal chemistry Pedro F. Pinheiro, Gonçalo C. Justino and M. Matilde Marques	IF2
NMR: a support technique at CQE Maria João Ferreira, José Ascenso, Pedro Pinheiro and Gonçalo Justino	IF3
Mass Spectrometry Facility at Instituto Superior Técnico Maria Conceição Oliveira and João Paulo Leal	IF4

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Abstract
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PL1

On Being a Scientist

Calado, Jorge

Abstracts
Keynotes

KNL1

Chemical Toxicology: from the minimization of chemically induced adverse effects to the development of diagnostic tools

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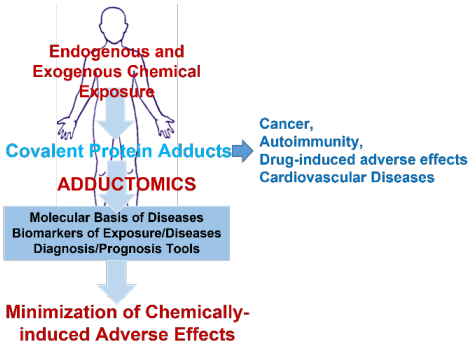
The role of Chemical Toxicology was highlighted by the United Nations 2030 Agenda, when the goal of "*substantially reduce the number of deaths and illnesses caused by hazardous chemicals and air, water and soil and contamination"*, was established. In fact, it is widely accepted that **chemical agents of endogenous, drug, dietary, occupational, or environmental exposure are associated with** a wide range of deleterious health outcomes, including cancer, cardiovascular and autoimmune diseases. However, t**he inability to avert most of these** adverse effects, by effective regulatory measures, reflects the difficulty in accurately assessing human exposure to chemical toxicants and classifying chemical agents' toxicological potential. This scenario can only be changed by the development of suitable analytical tools for the detection of more accurate biomarkers of exposure to chemical toxicants, necessarily involving further insights into the molecular basis underlying chemically induced toxic events.

It will be presented an overview of the chemical toxicology work performed during the last 15 years at the CQE, aimed at studying the role of metabolism&bioactivation and protein modification in the onset of chemically induced adverse effects, with direct application in the minimization of drug-induced toxic events,[1-3] the Identification of early biomarkers of chemically-induced cancers,[4-7] and the development of diagnostic tools.[8]



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KNL2

Smart hybrid polymer@silica nanocarriers for control release

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The ideal vehicle for smart delivery systems should be able to accommodate large payloads and feature a smart release control mechanism that allow the delivery of their cargo on-demand. These systems found application in precision agriculture, environmental remediation, corrosion control or drug delivery. In the latter case, the system should have two additional features: traceability (to follow the vehicle) and targeting (deliver the cargo at a desire location).

Our vision for the ideal vehicle for smart delivery systems is based in hybrid polymer@silica nanocarriers with a shell of responsive polymers and a core of silica nanoparticles. The core based in mesoporous silica nanoparticles (MSNs) offer high mechanical stability, well-defined particle morphology, tunable particle diameter and pore size (to accommodate the cargo), versatile functionalization (internal *vs.* external surface) and good colloidal stability. On the other hand, smart polymers can respond to a dynamic environment, with the fluctuation of stimuli over time inducing a modulated response of the polymer chain conformation and interactions activated by a trigger, such as temperature, pH, proteins, etc. This provides pore gating for active release control as well as modulate the interactions with the environment, and in specific applications improves biocompatibility and provides specific cell targeting.

First, a fully controllable low-temperature and purely aqueous sol-gel method to prepare MSNs with user-defined diameters from 15 nm to 80 nm and narrow size dispersity will be presented [1]. The method also allows modification of the pore structure and offers the possibility of incorporating a highly fluorescent perylenediimide [2] in the silica network for optical traceability. Control was achieved by tuning the colloidal stability of the assembly of cylindrical micelles that template the MSN synthesis.

Next, we will show how MSNs modified at the external surface with a polymer shell featuring conformational changes induced by temperature [3] or pH [4], can act as precise gatekeepers to control cargo release from the MSNs pore system. The nanoparticles feature either a polymer brush or a gel-like responsive shell, produced by grafting-from RAFT polymerization that offers low size dispersity [5]. Additionally, the internal surface was modified to interact preferentially with the cargo to decrease leakage in the “off” release state. In a different approach, we have developed hybrid polymer-silica nanoparticles based on a polymer shell of biocompatible poly(lactide-*co*-glycolide) (PLGA) grown by surface-initiated ring opening polymerization (ROP) from a fluorescent silica core, allowing the release of anticancer drug doxorubicin through selective cell-triggered PLGA enzymatic degradation [6].

The communication will include future perspectives for the field and possible strategies to leverage the potential application of these nanomaterials.

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KNL3

Novel approaches to fight metastatic cancer: the journey from small molecules to smart metallodrugs

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Metastatic cancer is one of the biggest burdens in society. Although treatable when early diagnosed, advanced or metastatic cancers are incurable and patients face a median survival time of less than 5 years, due to the lack of effective therapies. Indeed, current treatments are unspecific, unable to reach metastases, and show severe adverse effects mostly due to poor selectivity for cancer cells over healthy tissues. This scenario claims urgency in finding an effective solution[1].

Our group is currently working on developing novel smart metallodrug delivery systems (SMDS) capable of hunting both primary tumours and metastases, to provide society with a precision therapy for metastatic cancer that overcomes the limitations of antineoplastic drugs in clinical use. These systems promote selective accumulation and controlled release of a cytotoxic metal complex only at its local of action, resulting in increased therapeutic efficacy and reduced adverse effects/off-target action. The SMDS comprise a cancer-targeting peptide that recognizes with high affinity the fibroblast growth factor receptor (FGFR) often overexpressed by metastatic cancer cells, tethered to a known metal-cyclopentadienyl complex through a linker responsive to the acidic tumoral microenvironment. The latter allows site- and time-specific release of the active species into the tumour (Figure 1). In this communication, it will be presented our most recent findings on the design of multifunctional anticancer metallodrugs, from small metal complexes to advanced tumoral microenvironment-responsive metal-peptide conjugates[2].

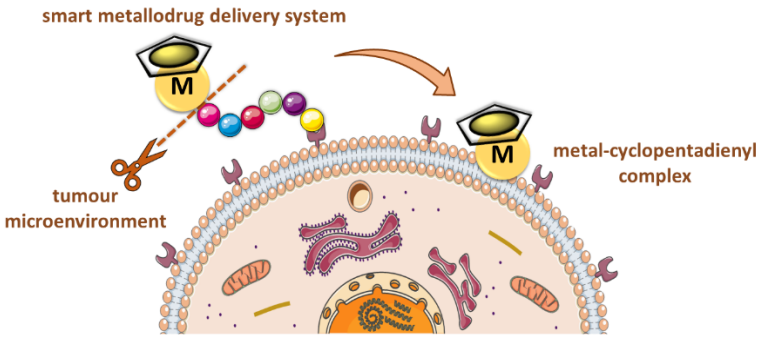

Figure 1. Proposed mechanism of action of the novel smart metallodrug delivery systems.

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KNL4

KNL5

Exploring the potential of late transition metal complexes toward olefin, carbonyl, and carbon dioxide reduction

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The reduction of carbon-centered substrates has copious implications in chemical sciences, while also carrying substantial socioeconomical impact. Among the many ways of achieving such organic transformations, hydrogenation is perhaps the most common, yet hazardous pathway [1]. With the advent of metal-catalyzed hydrofunctionalization [2], milder, more versatile, and selective ways to chemically reduce carbon-centered substrates have been found.

Hydrofunctionalization reactions such as hydroboration or hydrosilylation respectively provide structurally differentiated organoboron or organosilicon compounds, which are very interesting synthetic feedstocks, being crucial in the synthesis of many added-value compounds, from pharmaceuticals to products of the silicone industry or even key C1 building blocks [3]. Most significantly, hydrofunctionalization reactions have recently acquired added importance because of their potential to functionalize carbon dioxide, a greenhouse gas of ever-increasing proportions which undesirably disrupts the global water cycle [4].

Since hydrofunctionalization reactions are commonly catalyzed by expensive and toxic platinum group-based catalysts, it is important to develop cheap and abundant mediators [5]. In line with this, the hydrofunctionalization of carbon dioxide to methanol utilizing earth-abundant homogeneous catalysts is still a relatively recent approach that promises to avoid harsh operatory conditions while maintaining high reaction selectivity and low costs [6].

This Keynote shall highlight several works concerned with the hydrofunctionalization of numerous functional groups. A set of readily accessible, active, selective, and inexpensive catalyst systems for hydroboration and hydrosilylation of alkenes, carbonyl groups, and carbon dioxide based on rationally designed late transition metal complexes shall be discussed [7]. This approach provides new platforms toward more efficient production patterns, as well as responding to the current demand to mitigate the impacts of climate change.

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KNL6

Marine resources: discoveries and alternatives with future in Technological Chemistry

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With the objective of a sustainable society powered by solar energy in 2050, it is urgent to achieve studies in this direction and focus our efforts on the new trends in the evolution of our society and our economy. It is still necessary to gather these requirements with the use of sustainable chemical products, free of environmental and human risks, but necessarily efficient in their technological functions. With full awareness of the scarcity of some raw materials, the right decision-making will be based on increasing parameters in circular economy and minimizing waste.

This brief keynote presents some innovative solutions with marine resources in heat transfer and storage, in pigments for solar paints and in the replacement of fishing nets made with food waste transformed with ionic liquids into biodegradable yarns alternative to nylon.

In the conservation and sustainable use of the oceans, seas and marine resources for sustainable development, innovative methodologies are presented in the use of cuttlefish ink, shrimp shells and jellyfish in an intimate connection with thermal solar collectors [1], heat transfer fluids [2], fishing nets alternatives [3] and additives to polymers.

This demonstrates that it is possible to bet on new sources of raw materials, changes in the production and use of chemical products to guide us towards a naturally more sustainable future.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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KNL7

Data-Driven Prediction of Bioorthogonal Reactions

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Bioorthogonal reactions have become widely used for probing and controlling biological functions through labelling, tracking and imaging of biomolecules.[1] Ongoing developments in the bioorthogonal toolbox have resulted in improved reaction efficiency, selectivity and applicability, which continues enabling the design of innovative theragnostic and delivery systems for in vivo applications.[2] Fundamental determination of reaction kinetics in bioorthogonal chemistry is commonly performed by transition state analysis using density functional theory (DFT) calculations.[3] Herein we show a complementary, modern data-analysis approach by parametrizing the cycloaddition reagents and solvents[4] for modelling reaction rates of the inverse electron-demand Diels–Alder reactions[5] and the metal-free 1,3-dipolar cycloadditions[6].

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. J.A.S.C. thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND.

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KNL8

Climate change in the Arctic: Chemistry as a crucial tool to measure, understand and mitigate

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Temperatures in the Arctic continue to rise at three times the global annual average, driving many of the changes underway. Most prominently, snow and ice are melting at an increasing rate and permafrost is rapidly thawing. This impacts both local ecosystems and the global climate system.

Many of the observed changes are strongly related with biogeochemical process that occur in the North. For instance, the emission of greenhouse gases from thermokarst lakes are a consequence of the higher or lower lability of natural organic matter that also strongly influences contaminant dynamics. Moreover, the release of natural organic matter from permafrost thaw also has a profound impact in Indigenous Communities: from the collapse of infrastructures to the access to drinking water.

In this presentation, some of these aspects will be discussed pointing out the importance of chemistry not only to understand the chemical processes in the changing Arctic but also to investigate new solutions to mitigate the impacts.

Abstracts
Oral Presentations

O1

Cell adhesion and associated functions are dependent on a strict regulation of TBCCD1 levels

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Centrosomes are composed of two centrioles surrounded by pericentriolar material and, by nucleating/organizing both the microtubule (MT) and actin cytoskeletons, control the spatial organization of the cytoplasm, are involved in cell motility, adhesion, polarity, and cell division. The centrosome is also crucial for cilia formation. Primary cilia are specialized microtubule (MT)-based signaling organelles that convey extracellular signaling and cellular polarity into a cellular response. Defects in primary cilia assembly/function cause a group of severe diseases designed by ciliopathies.

We have characterized for the first time a centrosomal protein TBCC domain-containing (TBCCD1) that is involved in centrosome positioning, Golgi apparatus organization primary cilia assembly and cell migration [1]. A tight regulation of TBCCD1 levels is required to maintain/assemble specialized structures of the distal region of the older centriole involved in MT anchoring and organization with impact in cytoplasmic architecture and the anchoring of the primary cilia basal body during ciliogenesis. Using (BioID) we screened for TBCCD1 interactors and found 82 proteins that can be grouped into 5 functional groups: centriole/centrosome structure and cilia assembly, Wnt signaling pathway, cytoskeleton organization and cell division.

To get a wider view of how TBCCD1 changes lead to specific biological phenotypes we decided to investigate the impact of altered levels of TBCCD1 in cellular physiological proteome. For this we determined the proteomic profile of the RPE-1 cell line constitutively overexpressing TBCCD1-GFP and compared to that of RPE-1 cells. Our preliminary results show that a group of 41 proteins change their levels in cells in response to TBCCD1 overexpression. Considering the group of proteins showing fold changes in their levels vs control cells higher or lower than 2.5 times we found an enrichment in proteins involved in focal adhesions, namely HSPA5/GRP-78/BiP, PDIA3, RPS10, MSN,TGM2 and PPP1R12A. In this group MSN (Moesin a protein that binds actin cytoskeleton to the plasma membrane) showed an accentuated decrease in its levels (~42 times), while TGM2 was the only protein to present an increase of ~4 times. It is interesting to refer that in the above mentioned group of proteins HSPA5/GRP-78/BiP and PDIA3 are endoplasmic reticulum proteins involved in protein folding. These results show that we are still far from having a complete picture of the functional importance of TBCCD1 and how its deregulation may be associated with the loss of cell homeostasis, namely in the process of cell-substrate adhesion, intracellular transport and protein secretion which may have implications in carcinogenesis.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Funds are also from Instituto Politécnico de Lisboa, IPL/2021/ObeCil_ESTeSL and IPL/2022/WintCilGlu_ESTeSL.

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O2

Repurposing montelukast for Alzheimer's – a proteomics assessment of a new *in vitro* neuron model

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Montelukast, a leukotriene receptor antagonist commonly used to treat asthma, has been identified to be an inhibitor of other receptors and enzymes, suggesting its potential for repurposing in neurodegenerative diseases such as Alzheimer's disease, Parkinson's disease and Huntington's disease. A re-analysis of proteomics datasets deposited in public repositories (data from mouse brain and a neuronal chicken model exposed to montelukast) has been conducted to identify potential biological pathways affected by MTK that may support its repurposing for AD management.

The analysis revealed that montelukast works as a modulator of the amyloid clearance process, favoring the removal of aggregates and counterbalancing the overall amyloidogenic process which is a hallmark of AD. Additionally, that MTK also may modulate inflammatory and apoptotic pathways involved in neurodegenerative features, including those mediated by TNF-α, NF-κB, caspase-3, Bcl-2, MAPK, and IL-1β. Furthermore, MTK appears to decrease α-synuclein load and Aβ1-42 induced neurotoxicity, as well as modulate oxidative stress associated with redox homeostasis dysregulation. Montelukast is suspected to play a role in maintaining energy homeostasis in the brain. Specifically, montelukast was found to compensate for the aging-associated decrease in basal cell metabolism. This indicates that montelukast may have a protective effect on cellular energy metabolism, which could contribute to its neuroprotective effects in AD.

These results provide insights into the potential mechanisms underlying MTK's effects in neurodegenerative disorders and support further investigation of MTK as a repurposing candidate for AD management.

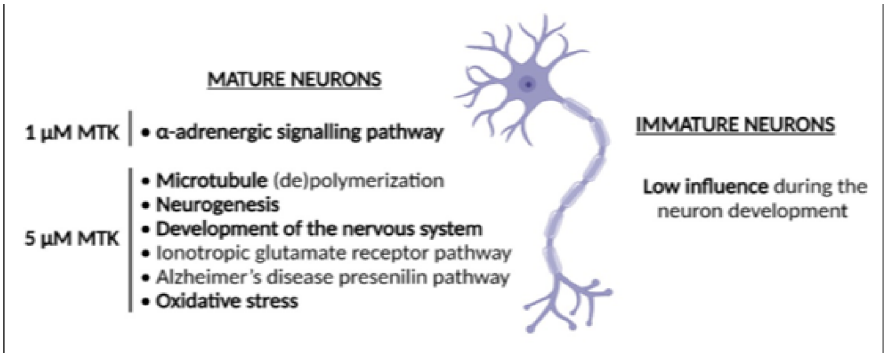

Figure 1. MTK effect on the biological processes in an *in vivo* chicken neuron model in different maturation stages.

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O3

Peptide-eluting contact lenses enhance topical drug delivery across the ocular barriers

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Intraocular injections are the current treatment of pathologies affecting the posterior segment of the eye. However, they are invasive and associated with side effects. Eye drops, on the other hand, have a low bioavailability and a massive drug loss by lacrimation. An emerging approach is the use of contact lenses (CL), which could load and deliver drugs in a sustained fashion, increase the drug residence time on the cornea and therefore its bioavailability. However, when targeting the back of the eye, drug released from contact lenses still encounters the barriers of the ocular tissues, which significantly reduce the efficiency of delivery. Peptides have been recently proposed as carriers for cargo drugs across biological tissues. Herein, the possibility of producing hydrogel-based CLs, simultaneously loaded with Penetratin (PEN), a cell-penetrating peptide, and an anti-inflammatory drug (dexamethasone sodium phosphate, DexSP), was evaluated. Besides HEMA (*H1 hydrogel*), chosen as the backbone monomer, also acrylic acid (AAc, *H2 hydrogel*) and aminopropyl methacrylamide (APMA, *H3 hydrogel*) were added into the CLs polymeric mixture as functional monomers with a high affinity for PEN and DexSP, respectively. *H4 hydrogel* included both AAc and APMA. After polymerization, hydrogels were loaded by soaking in a dual solution of peptide and drug. *In vitro* release and physical characterization were performed. Then, *in vivo* tests were carried out on rabbits to evaluate the efficacy of the strategy in enhancing DexSP delivery. *H3 hydrogel* successfully loaded the peptide and drug and simultaneously released them for at least 7 hours, which is compatible with the wearing time of daily CLs (Figure 1). The light transmittance and liquid uptake of the hydrogel resulted adequate for CL materials. *In vivo* tests revealed an increase ($p < 0.05$) in the amount of DexSP detected in the cornea and aqueous humor when delivered in the presence of PEN. The obtained results shall provide a therapeutic effect in the back of the eye with no need for injections.

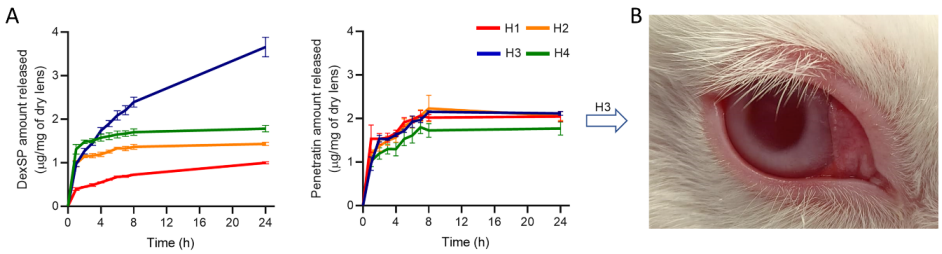

Figure 1. *In vitro* drug release profiles of DexSP and Penetratin (A); H3 hydrogel was selected as the most promising CL material and was tested *in vivo* (B);

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the MSCA GA N° 813440 (ORBITAL), and by FCT through N. Toffoletto PhD Grant 2022.10004.BD and the project SOL (PTDC /CTM-CTM/2353/2021).

O4

A new ruthenium-cyclopentadienyl compound as a promising cancer MDR reversing agent

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Accounting for nearly 10 million deaths in 2020, cancer ranks as the 2nd leading cause of death worldwide. Despite the recent advances made in the treatment of some types of cancer, when it relapses, it usually does not respond to such treatments anymore. This problem, known as multidrug resistance (MDR), is a challenge that researchers and clinicians seek to understand and overcome and has several mechanisms, where the expression of transport proteins (*e.g.*, P-glycoprotein (P-gp) and Multidrug Resistance Protein 1 (MRP1)) are major players. We have recently disclosed the potential of a family of organometallic ruthenium(II) compounds with remarkable anticancer activity against several cancer cell lines[1] and unveiled them as possible ABC transporters inhibitors.[2],[3] Importantly, it was also shown that some compounds were only cytotoxic to the cells overexpressing ABC transporters. From this perspective, we have been targeting this "Achilles' heel" to treat resistant cancer cells, sparing the healthy ones, and overcoming undesired toxic side-effects. Among the twelve compounds tested against four types of non-small cell lung cancers (NSCLC) with different rates of chemoresistance and expression levels of P-gp and MRP1 transporters, one stood out as a lead. In this presentation, we will present several *in vitro* and *in vivo* studies supported by molecular docking calculations which highlight the potential of RT151 ($[Ru(\eta^5\text{-}C_5H_4CH_2OH)(Me_2bipy)(PPh_3)][CF_3SO_3]$, where Me_2bipy is 4,4'-dimethyl-2,2'-bipyridine) as a potent antitumor drug and as an alternative to classical chemotherapeutics used in the clinic.

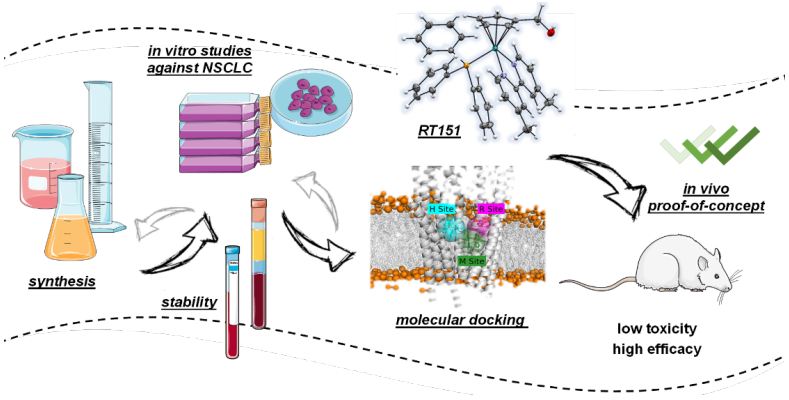

Figure 1. Development of ruthenium(II) compounds as potential MDR reversers.

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O5

Stimuli responsive surfactants: towards smart templates for mesoporous silica nanoparticles

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Mesoporous silica nanoparticles (MSNs) feature unique characteristics that make them useful in many applications. Novel MSNs with a dual pore system, containing two distinct pore types that can carry and independently deliver different cargo selectively, would open ever greater possibilities in fields such catalysis, sensing, energy, biomedicine, etc. To develop dual pore system MSNs an innovative strategy is to use a system of two surfactants that do not form mixed micelles and could be selective removed allowing selective pore functionalization and control release.

In this work, our objective was the development of novel cleavable surfactants that can be used as smart templates in the synthesis of MSNs and selectively removed through a specific stimulus. Our vision was to prepare a redox responsive surfactant, containing a disulphide bond as linker, to take advantage of its reactivity in the presence of a small size reducing agent, such as dithiothreitol (DDT) or its analogues.

The new redox responsive surfactant (CTAB-SS) was successfully obtained and preliminary studies confirm the potential to be used as smart surfactant. Degradability tests show that, after 30 minutes in the presence of dithiothreitol (DTT), occurs the cleavage of the S-S bonds, since it was possible to observe the characteristic absorption band of ox-DTT at 283 nm, which is a product of the reaction of DTT with the disulfide bond of CTAB-SS. An estimate critical packing parameter of CTAB-SS was obtained from its optimized structure, and the result indicate that CTAB-SS will form cylindrical micelles, due to the structure similarity with CTAB. The surface tension of a set of solutions of CTAB-SS was measured using the pendant drop method, however the results were not conclusive on the behavior of CTAB-SS in solution and was not possible to determine the critical micelle concentration. Dynamic light scattering measurements reveal the presence of particles with 47 ± 5 nm of mean hydrodynamic diameter, which, if cylindrical micelles are formed as predicted by the cpp, correspond to the formation of cylindrical micelles with a maximum length of 261 nm.

Overall, the results indicate that our goal was achieved with the preparation of a new smart surfactant (CTAB-SS), which will be a breakthrough in the field of mesoporous silica materials and in other fields, from surface modulation, to controlled drug release, detergency, and others.

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[3] Brown, P.; Butts, C. P.; Eastoe, J. Stimuli-Responsive Surfactants. Soft Matter 2013, 9 (8), 2365–2374.

O6

Smart self-healing polymer materials for supercapacitors

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Facing the current global scenario of high energy demand, there is a crucial need for the development of new materials capable of storing energy. Supercapacitors emerge as an alternative to usual batteries due to their high-power density, long life cycle and fast charge/discharge rate properties. In addition to its development and energy performance, thinking about new sustainable materials is extremely important.

In this sense, manganese dioxide (MnOx) is considered as an outstanding pseudocapacitive material because of its earth-abundance, low-cost and environmentally friendly.[1] However, it can undergo irreversible phase transitions and degradation if exposed to extreme pH environments (pH < 4 or > 8) that occur due to electrochemical stress during operation, leading to device failure.[2] A strategy to overcome this issue and guarantee its power performance and life-time, is to use pH-responsive polymers capable of sensing local pH changes at the material level. The pH-responsive polymer shell would be responsible to expose/protect the MnOx through changes of the chain's conformation. In neutral form, the polymeric chains are collapsed protecting the material. After protonation/deprotonation the chains expand due to electrostatic repulsion and the material is exposed to the electrolyte.

In this work, we prepare by free radical polymerization two new pH-responsive co-polymers based in acrylic acid (AA, pKa_{AA} = 4.6) and diethylaminoethyl acrylate) (DEAEA, pKa_{DEAEA} = 9.2). In both cases, a cationic monomer was added, acryloyloxyethyl trimethyl ammonium (AETMA), to ensure the adsorption of the co-polymers chains onto the negatively charged MnOx surface through electrostatic interactions. The new co-polymers, PAA/PAETMA and PDEAEA/PAETMA, were characterized by NMR and GPC-MALS, and the pH transitions were measured by UV-VIS spectroscopy (Fig.1). The preliminary results of the incorporation of these co-polymers as protective material in MnOx electrodes are promising, demonstrating the reversible mechanism of protection of the active particles, with a loss of only 4 % of capacitance after 3 consecutive stresses, while the bare MnOx completely loose the performance immediately after the first electrochemical stress. Such results open perspectives for the development of a new set of composites for the next generation of self-healing energy storage devices.

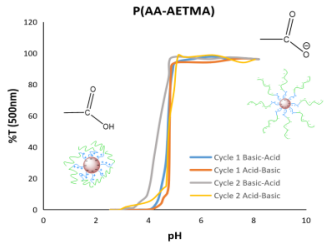

Figure 1. Transmittance *vs* pH of co-polymer P(AA-AETMA) by addition of 0.2M NaOH and 0.2M HCl.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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O7

CO_2 mineralization using industrial solid wastes

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Climate change is one of the biggest challenges in modern society. CO_2 accounted for roughly 74% of greenhouse gas (GHG) emissions in 2021 [1]. Mineral carbonation is a natural weathering process that regulates atmospheric CO_2 levels by the formation of carbonate rocks. Accelerated mineral carbonation via enhanced weathering is a CO_2 removal strategy that can be used by industries that generate alkaline wastes, such as iron and steel slags, coal fly ashes and incinerated municipal solid wastes. This methodology is considered one of the most promising technologies to stabilize solid wastes while fighting global warming by capturing CO_2. Several routes can be used however, a direct gas-solid contact route presents several limitations, namely slow reaction rates [2]. On the other hand, aqueous routes can be used in two different ways: either with a slurry solution, where the CO_2 is dissolved in the aqueous solution and reacts with the alkaline earth metal ions (Ca^{2+} and Mg^{2+})[2], precipitating via carbonate compounds as, per the principle of Le Chatelier, the ions present in the solid waste will dissolve in water allowing the further reaction to take place [3]; or via an indirect route, with the initial leaching of the ions through contact with a solvent (usually acids or ammonia salts). This method may be limited by the solubility of the ions in water [4].

This work focuses on mineral carbonation using a direct aqueous route. A set of batch experiments were carried out on a 100 mL reactor with magnetic stirring at the desired pressure, using pure CO2 and an aqueous solution of $Ca(OH)_2$ as reactants (Figure 1). Several batch tests were carried out with a total duration of 60 minutes, with different initial CO_2 pressure (10-20 bar) and $Ca(OH)_2$ concentration (1-20 g/L), for studying the effect of the initial CO_2 pressure and Ca^{2+} (aq) concentration on the carbonation efficiency. After ending the batch experiments, 2 mL of NaOH (2 M) were added to the solution to further increase the precipitation of the carbonate.

The results show that a complete conversion of $Ca(OH)_2$ is obtained for all the experiments with the formation of $CaCO_3$ precipitate and the final step of adding a strong base leads to an increase of the amount of $CaCO_3$ precipitate from 74% to 96%, after ending the batch carbonation at the reactor. A higher initial $Ca(OH)_2$ concentration increases the reaction rate. Based on the experimental methodology used, the CO_2 pressure on the reactor gas phase has a relevant effect on the carbonation reaction rate but it doesn't seem to have a significant effect on the final carbonation efficiency obtained.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. The authors thank Professor Miguel Rodrigues for making the experimental set-up available for the carbonation experiments and for the support shown to this project. Authors also thank the FCT for funding the project "SoCaLTES: Solar-driven Ca-Looping Process for Thermochemical Energy Storage" (PTDC/EAM-PEC/32342/2017).

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O8

Assessment of biomass-derived GACs for point-of-use water filters

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Proper water quality is essential for human health and several industrial and laboratorial procedures. Point-of-use (POU) water filters have been increasingly adopted by final consumers to improve tap water quality (e.g., removal of color, taste & odor compounds or organic microcontaminants), particularly when they are served by old or compromised water distribution systems. POU devices hold a market value of around 30 billion dollars annually and are estimated to have an annual growth of 7.5% in 2023.

Aiming to develop improved POU devices, tailored granular activated carbons (GACs) prepared from pine-nut shell (PNS) [1] are being tested using batch adsorption tests (kinetic and isotherms) and rapid small scale column tests (RSSCTs) to assess their efficiency on dissolved organic matter (DOM, measured as total organic carbon and as absorbance at 254 nm) and residual chlorine removal from tap water. PNS/GACs were prepared by steam or CO_2 activation and sieved to obtain fractions with adequate particle size distribution for the RSSCTs and POU filters. PNS/GACs surface chemistry properties were assessed and each fraction was characterized regarding the nanoporous structure. The lab-made materials were benchmarked with a commercial golden standard of mineral origin (F400, CalgonCarbon).

All lab-made GACs were significantly more alkaline than the mild acidic F400 (>9.5 vs 5.8). Porosity was also larger when compared to F400 (BET area 1309-1706 m^2/g vs 1314 m^2/g). So far, batch tests results show that PNS/GACs outperform commercial F400 for DOM adsorption, with the steam activated PNS/GACs attaining the higher removal efficiencies.

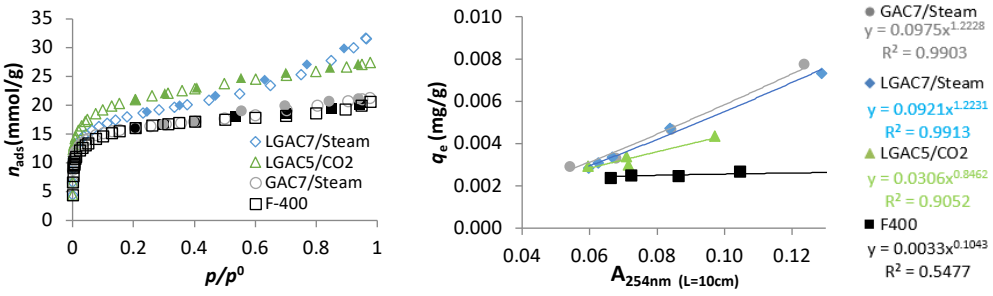

Figure 1. N_2 adsorption isotherms (left) and DOM (as A_{254}) adsorption isotherms (Freundlich model) (right).

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O9

Fatty acids-based Eutectic Solvents Liquid Membranes for Removal of Micropollutants from Water

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Pharmaceuticals have a main role on health and life quality of humans and animals. Nevertheless 30% to 90% of all oral administrated drugs are excreted as active compounds, leading the worldwide occurrence of these active compounds and their metabolites in water sources, soils, and biota. As these compounds are designed to have a biological response to small dosages, they are an important threat to public health and ecosystem stability even at low concentration [1]. Additionally, their relative high stability is even more concerning, as the continuous ingestion of small doses can lead to accumulation since the degradation rate is slower than the up taking. On the other hand, conventional wastewater treatment plants (WWTP) are not designed to remove these compounds that enter the environment. Despite the report of diverse cases of life-threatening biological effects of these drugs on wildlife, about 88% of all pharmaceuticals do not have environmental toxicity data [2].

Although the use of eutectic solvents (ES) provides a cheap and efficient solution for the removal of APIs micropollutants [3 – 4], the toxicity of some of the used compounds and their leaching are drawbacks that need to be overcome to develop a fully sustainable system. The use of all natural compounds like sugars, amino acids, organic acids, choline and urea that exhibit low toxicity and have a high biocompatibility might be the answer for this problem.

In this work, ES based on fatty acids were impregnated on porous membranes by soaking and used to remove sodium diclofenac from water using UV-Vis spectroscopy to quantify the extraction efficiency of the membranes. Experimental parameters such as contact time, number of membranes, pH and initial concentration of pharmaceutical were optimized to achieve a remarkable extraction efficiency 97%. These membranes were re-used over 9 more cycles of extraction without decreasing the efficiency.

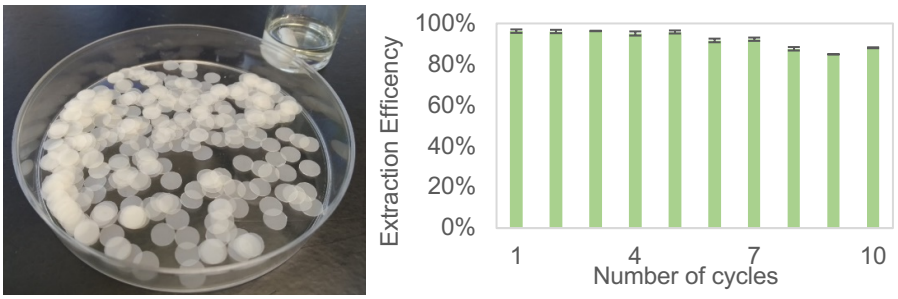

Figure 1. Liquid membranes used for micropollutant removal (Left). Extraction efficiencies of 10 extraction cycles of sodium diclofenac solution (Right).

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O10

On Capillary Viscosity Measurements: How Far do Surface Tension Effects go?

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Viscosity is a fundamental thermophysical property of liquids making it very important particularly in the industry. Capillary viscometers have been widely used for viscosity measurements in different applications, the most relevant being the definition of viscosity standards, traceable to the primary water viscosity standard, by metrological institutions and industrial applications, mostly for quality control. Practical viscometry is based on the internationally accepted primary standard value for the kinematic viscosity of water at 20ºC and atmospheric pressure, which has been measured using capillary viscometers [1]. However, due to the water surface tension, viscosity measurements which have been related to water as a primary standard, can be significantly affected. It is difficult to rigorously assess the surface tension effects on capillary viscometers, and the practical way to avoid this problem is to use long capillaries, which are not appropriate for routine measurements [1-3]. After several experimental studies, using different types of viscometers, the usual procedure to correct surface tension effects in capillary viscosity measurements adopted by different authors, is to employ an empirical expression [1-4]. Additionally, other types of problems exist as the need to perform a kinetic energy correction which must also be taken into consideration [1].

The main goal of this work was to perform the calibration of a suspended-level, or Ubbelohde, capillary viscometer, which is not a long capillary viscometer, as well as the study of corrections to be used for the measurements performed with it.

The experimental work covers the calibration of that Ubbelohde capillary viscometer, the evaluation of the uncertainty of the corresponding viscometer constant and the overall uncertainty of the measurements performed with it. This study includes the evaluation of the necessary corrections for kinetic energy and surface tension effects and, finally, the analysis of the case of a set of measurements performed with n-tetradecane.

The ultimate purpose of this work is to obtain the lowest uncertainty for the Ubbelohde capillary viscometer 541 01/Ia, and to understand the need for the corrections that must be considered when using capillary viscometers and how they should be applied.

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O11

Pressurized liquids to obtain DHA enrich extracts from microalga *Crypthecodinium cohnii*

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Microalgae have emerged as a promising feedstock to produce biofuels and ω-3 compounds, which have important applications in the food and pharmaceutical industry [1]. The marine microalgae *Crypthecodinium cohnii* (*C. cohnii*) is a non-photosynthetic heterotrophic dinoflagellate that can be found in tropical and temperate waters worldwide [2,3]. This oleaginous microorganism is capable of accumulating significant amounts of lipids (up to 50% of its dry weight), with a high fraction of docosahexaenoic acid (DHA), a polyunsaturated fatty acid (PUFA) of the ω-3 group.

The present work aimed to explore the use of an environmentally friend technique, pressurized liquid extraction (PLE), using two biobased solvents: ethyl acetate and 2-methyltetrahydrofurane, to obtain lipids from *C. cohnii* and to implement a simple and environmentally friendly process for the co-production of biofuels and the high added-value product, DHA. With the purpose of optimizing the experimental extraction conditions for the maximum yield, an experimental design based on a surface response methodology, according to the Doehlert distribution for two factors, was built [4,5]. The evaluated factors were temperature (40-200 °C) and the time of extraction (2-20 min), being the response factors the yield in total fatty acids (TFA) and in DHA. It was observed that the time and temperature had little influence in the yield of extraction, being that time shows almost no influence. DHA in TFA for ethyl acetate is almost invariable. TFA yield is almost the same for every condition using 2-methyltetrahydrofuran, meaning DHA content in the extract can be controlled by changing the factors. Overall, mild conditions yielded satisfying results, for both solvents and 2-methylhydrofuran was the solvent that allowed to reach the higher yield (26 g/100g $_{\text{ash free dry biomass}}$)

The isoresponse surface graphics allowed to determine the range of time and temperature in which the highest yield could be obtained. For the case of 2-methyltetrahydrofuran the maximum yield in TFA was attained in the upper left quadrant of the graphic, corresponding to the highest temperatures and lower times of extraction. Finally, for DHA the isoresponse surface graphic showed diagonal symmetry, meaning that the highest yield was obtained in the upper left quadrant, as well as in the lower right quadrant, showing that the efficiency of extraction is higher at high temperatures and low extraction times, or at low temperatures and high extraction times.

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O12

Validation of physical-chemical tests of solid biofuels for the international accreditation of analytical capabilities

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The last decades have been characterized by a significant increase in the demand for new alternative energy sources of fossil fuels due to their depletion in nature and their greenhouse gas production [1]. One of the emerging sources of renewable energies is solid biofuels, which include solid non-fossil materials of biological origin (biomass), that can be obtained from charcoal, wood residues, and animal waste, among others [2]. Faced with this scenario, EDP Labelec decided to adapt the equipment and methodologies, previously used to analyze coal, for the analysis of solid biofuels.

The present work describes the development of methods to analyze important parameters of solid biofuels and carry out these methods' validation, with the objective of obtaining accreditation by IPAC. Elemental analysis was implemented to determine the content of carbon, hydrogen, nitrogen, and sulfur and consequently, the oxygen content was calculated. By thermogravimetric analysis, the inherent moisture and ash contents were determined, and the volume-constant calorimetry allowed the determination of the higher calorific value. When all the analyses were carried out, the lower calorific value was calculated. All the developed methods were based on ISO standards.

It was possible to successfully conclude the validation process of the different methods and to obtain reliable results that meet the established criteria, namely the repeatability, uncertainty of the measurement, and proficiency tests. The results were proven by the analyses of synthetic certified reference materials (CRM).

In terms of elemental analysis, it was not possible to produce a calibration curve for carbon that fulfills the linearity test criterion however, we were able to get a high correlation coefficient making the curve sufficiently satisfactory on a practical level. The content of sulfur and nitrogen in the sample was not within the calibration working range.

Due to the unavailability of a CRM with the biomass matrix, it was not possible to confirm that the developed methods are suitable for the purpose making it impossible to verify the influence of matrix effects in the results.

Nonetheless, given the availability of the equipment and the material, the carried-out procedure was successful.

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O13

Nanofibers of $LnInO_3$ perovskites (Ln= La, Pr, Sm, Dy and Yb) as catalysts for the Oxidative Coupling of Methane

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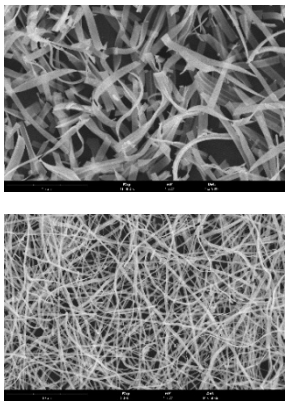
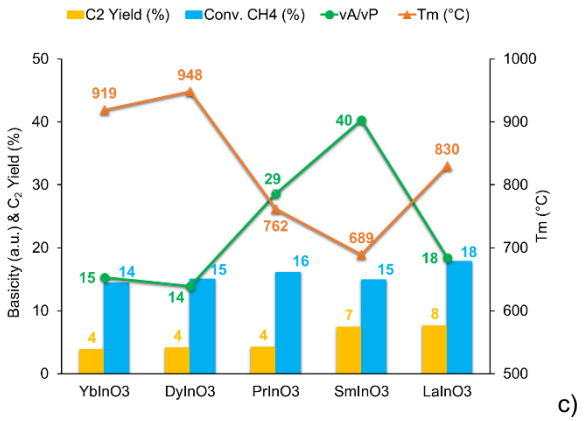
Methane and nitrous oxide are by-products that arise from industrial processes with a notorious harmful impact on the environment, far superior to that of carbon dioxide. [1] Nevertheless, methane is a known player in the energetic sector and nitrous oxide has proven to be a valuable reactant in some oxidation processes, such as oxidative coupling of methane (OCM). [2] Moreover, OCM is a highly promising pathway for converting methane into higher hydrocarbons, namely C_2 hydrocarbons (ethane and ethylene). However, the development of highly active and inexpensive catalysts with high temperature stability remains a major challenge yet to be achieved. [3] Perovskites, of the type ABO_3, have attracted attention as promising catalysts for many catalytic reactions, such as hydrogen-involving reactions, water splitting and methane valorisation. [4] Their physical and chemical attributes, such as good thermal and structural stability and high oxygen mobility, contribute significantly to their excellent performance. [5]

The main objectives of this work were the synthesis and characterization of indium-based perovskite nanofibers containing lanthanides, $LnInO_3$ (Ln = La, Pr, Sm, Dy and Yb) and the study of their efficacy as catalysts for the conversion of methane into C_2 hydrocarbons using nitrous oxide as an oxidizing agent. Figures 1a and b show selected SEM images of the obtained nanofibers. Figure 1c shows the influence of the f-block element, namely their maximum reduction temperature (Tm) and basicity on the $LnInO_3$ nanofibers catalytic performance for OCM. Clearly, $LaInO_3$ and $SmInO_3$ exhibit the best yields in C_2 hydrocarbons. The catalysts' reducibility and acid-base properties seem also to contribute to the catalytic behaviour along the lanthanide series. The combination of a higher lattice oxygen mobility (lower Tm) and higher basicity enhances the catalysts activity, except in the case of La.



a)

b)



c)

Figure 1. a) and b) SEM images of the nanofibers; c) Influence of the rare-earth element on the catalytic performance for the OCM (Reaction Conditions: GHSV=15000 mL/g_{cat}.h; T=700 °C; N_2O/CH_4=1).

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O14

Electrochemical Functionalization of Quinolizidine Alkaloid

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Quinolizidine alkaloids (QA) are largely abundant in the *Leguminosae* family, especially in the genera *Lupinus* [1]. Maulide and Afonso's groups developed processes for the extraction of lupanine from *Lupinus albus* seeds wastewater and for the preparation of sparteine from lupanine [2]. These natural products are known for their pharmacological activities, which includes antimicrobial, antihypertensive, antimuscarinic and antidiabetic, as hyperglycemia agents, effects on the central nervous system and uses in asymmetric organic synthesis [3]. Motivated by the potential added value of novel QA derivatives, we explored the selective C-H functionalization of QA using electrochemistry. Currently, chemists search for alternatives that follow green chemistry principles such as development of safer methodologies, waste prevention and reduction environmental impact [4]. In this context, we have been interested in the use of electrochemistry and continuous flow processes [5]. This modern electrochemical methodology offers an efficient and greener alternative to conventional oxidation/reduction procedures [6]. Herein we present a methodology for the cyanation of lupanine (**Figure 1**), in batch and flow, including reaction conditions optimization and discussion on guidelines for developing synthetic organic electrochemistry.

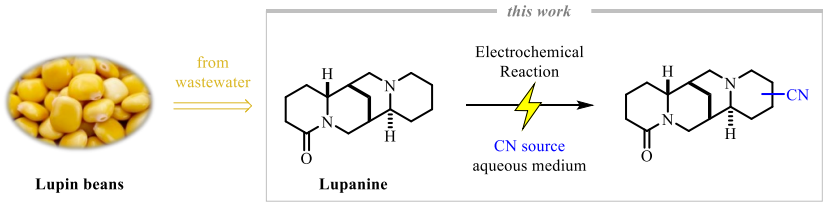

Figure 1. Electrochemical cyanation methodology. The electrochemistry equipment used in this work was an ElectraSyn 2.0 system by IKA.

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O15

Thermo- and Photo-responsive Spin Labile Fe(III) complexes

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Multifunctional materials can be used in a wide range of technological applications. These materials can be based on different types of molecules, such as metal complexes. Compounds displaying the spin crossover (SCO) phenomenon demonstrate different magnetic behaviour when exposed to an external stimulus, such as temperature, pressure, or the irradiation of light. One example of compounds displaying the SCO phenomenon are Fe(III) complexes with Schiff base ligands which can originate crystal with lability with photo and thermo-responsive properties. These thermo- and photo-responsive properties arise from their unique molecular structure, which allows physical changes by varying the temperature and irradiation with light. These changes affect their shape, volume, and mechanical properties originating flexible crystals that can transform light and heat energy into mechanical work directly.

Our approach consists in the production of mechanically responsive molecules with magnetic switching properties combining these mechanical effects with the SCO phenomenon in the same material using Fe(III) complexes. Here we report our findings on the production of Fe(III) SCO complexes with thermo and photosalient properties, which were characterized through optical microscopy.

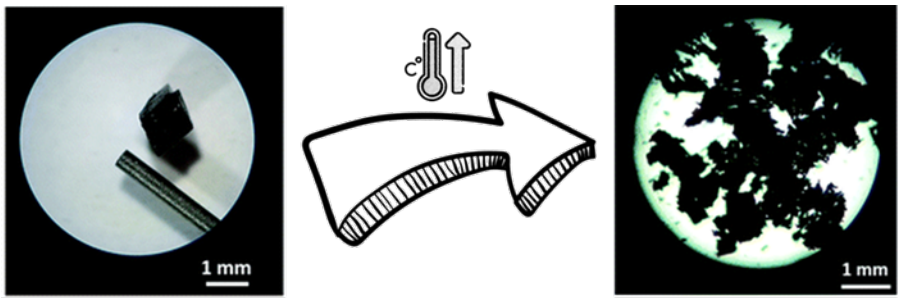

Figure 1: Thermosalient effect in an Fe(III) SCO compound.

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O16

Methyl- and phenylnickel complexes with triazole-tethered phenoxyimine ligands for the catalytic hydrosilylation of olefins

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The hydrosilylation of olefins is an important reaction in the silicon industry since it opens doors for organosilicon feedstocks that can be applied, *e.g.*, for the cross-linking of silicone polymers and to produce silicone rubbers, oils, or resins [1]. Although the most efficient and selective catalysts for this reaction are based on complexes of noble metals, more sustainable alternatives began to be explored to circumvent their high cost and toxicity. Complexes based on the earth abundant iron and cobalt metals have been studied as promising options in recent years [2], but nickel has algo fueled valuable contributions to this field [1-5]. The known (salicylaldiminato)methyl-nickel(II) systems, intensively studied as polymerization pre-catalysts, also exhibited good activities for secondary hydrosilanes, with high selectivity for the monohydrosilylated products [6]. Our group has a significant background in the development of Ni(II) complexes but mainly for polymerization [7,8]. Thus, we decided to broaden the range of catalytic applications. New *N,N,O*-tridentate ligand precursors containing phenoxyimine and triazole moieties were prepared by a multistep strategy, and the subsequent reaction with [Ni(TMEDA)Me_2], or the *in situ* deprotonation of the ligand precursors, followed by reaction with Ni(TMEDA)PhCl], respectively led to the methyl- and phenylnickel(II) complexes (***Cat.***). The catalytic application of the complexes was then explored in the hydrosilylation of several olefins, with all the complexes converting the substrates to its respective hydrosilylated products in yields in the range of 29-95% (Figure 1).

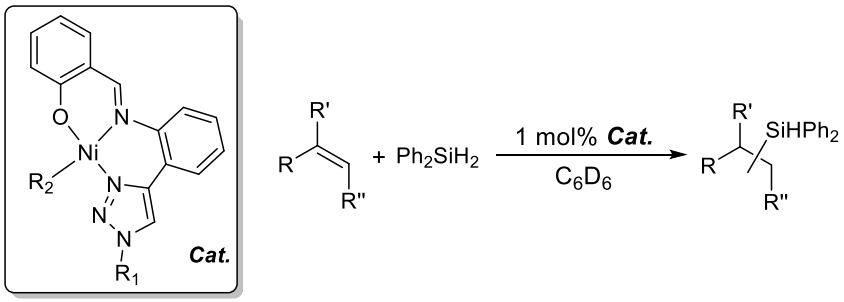

Figure 1. Hydrosilylation of olefins catalyzed by Ni(II) complexes (***Cat.***).

Acknowledgments: CQE is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. IMS is an Associate Laboratory funded by FCT through project LA/P/0056/2020. LAQV is a Research Unit and an Associate Laboratory funded by FCT through projects UIDB/50006/2020, UIDP/50006/2020 and LA/P/0008/2020.

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O17

Understanding the Thermal Conductivity of Ionic Liquids: A Direction to Select New Heat Transfer Fluids

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Ionic liquids (ILs) are salts in the liquid state at room temperature with some relevant properties, namely their low vapor pressure over a large temperature range, making them possible candidates for heat transfer applications. Among all known ILs, the ones with imidazolium-based cations are the most studied, given their safety, low cost, low viscosity, non-toxicity, and biodegradability. [1,2]

ILs are considered sustainable novel solvents in chemical technology. As such, there is a need to fully understand their properties. This work reports the thermal conductivity of the binary system water and 1-ethyl-3-methylimidazolium dicyanamide for all the composition ranges and the influence of the imidazolium-based cation's alkyl chain and different anions on this thermophysical property [3,4]. The thermal conductivity was measured with a transient hot-wire probe, in the temperature range 303.15 K < T < 348.15 K, un an estimated expanded uncertainty U_r (λ) = 0.02. [5]

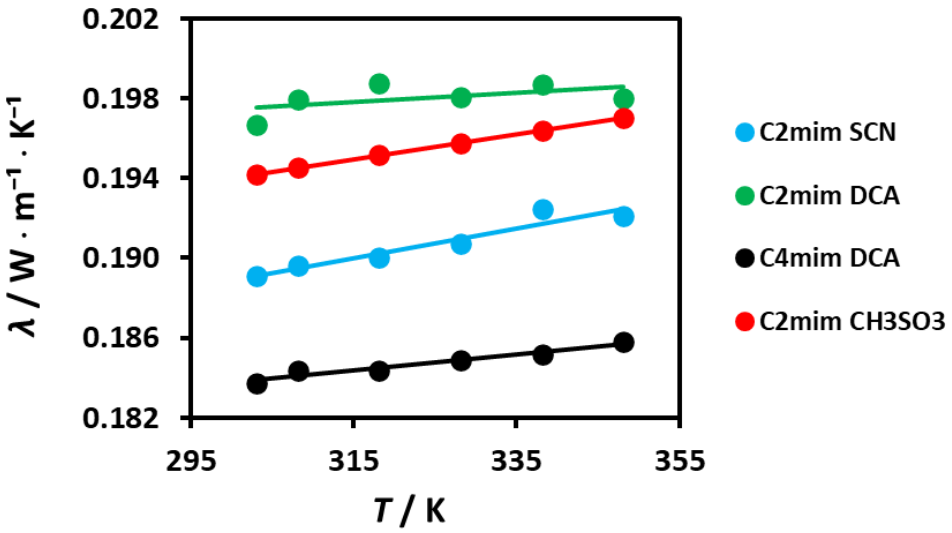

Figure 1. Thermal conductivity of [C_2mim][$N(CN)_2$], [C_2mim][SCN], [C_2mim][CH_3SO_3] and [C_4mim][$N(CN)_2$] as a function of temperature.

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O18

Perfluorinated (PFAS) Pollutants – Molecular Modelling and Simulation for Environmental Remediation

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Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds with exceptional characteristics of chemical inertness, simultaneous hydrophobic and lipophobic character, surfactant activity, among others. PFAS have thus found countless uses, from water- and oil-repellent surface coatings to fire-fighting foams. This widespread use, allied to the extreme chemical inertness, has led to the accumulation of these compounds in the environment and PFAS earning the epithet of “Forever Chemicals”. Although PFAS were initially considered biocompatible, studies have demonstrated their bio-accumulative potential and established links between exposure to PFAS and severe health issues including cancer. For this reason, states are issuing ever more restrictive legislation on PFAS production and use, and tightening the limits on their presence in food, water, and effluents. The number of PFAS remediation plants is thus growing rapidly in several countries and is expected to continue accelerating.

The current remediation processes require the removal of the perfluorinated pollutants from the contaminated matrix, for further destruction by other methods, and include adsorption on solids, membrane processes or flocculation. More recently the foam fractionation process has emerged as a novel method that separates PFAS by adsorption to the interface of rising air bubbles in a column of water, which form a concentrated foam at the top of the column and are extracted. Knowing the thermophysical behaviour of PFAS is crucial for the design and optimization of all these technologies but, however, large gaps and inconsistencies exist in the available experimental data, and development must still rely on trial-and-error.

In this work, a molecular modelling approach is used to gain a molecular-level understanding of the behaviour of PFAS. Molecular models and simulation methods are tested, validated against the available literature results, and then used to obtain properties for related compounds, extrapolate beyond the experimentally studied conditions or to provide reliable estimates of thermophysical data whenever experimental values are unavailable, disperse or inconsistent. Examples are presented for diffusion coefficients and for adsorption at the surface of water.

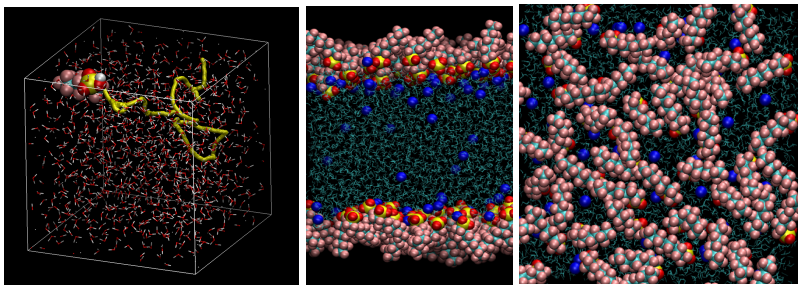

Figure 1. Left to right: 1 ns diffusion of perfluorohexanesulfonic acid in water; side- and top-view of a film of NaPFOS adsorbed at the surface of water.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

O19

Sustainability analysis and decision making of a Ca- Looping plant using water as fluidisation fluid for calcination

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Cement is at the forefront of economic development, and it is also one of the largest industrial contributors to CO_2 emissions, accounting for 8 % of global CO_2 anthropogenic emissions [1].

These emissions have two main sources, the limestone calcination, and the combustion of hydrocarbon-based fuels to achieve the required reaction temperature (900 ºC). Concentrated solar technology is a viable alternative to achieve the high temperatures required for calcination [2], which will allow reducing carbon emissions. Furthermore, the reversibility of the calcination of calcium carbonate (Calcium Looping (CaL) process) enables it to be used for thermochemical energy storage (TCES) [3].

The aim of this work is to make a sustainability analysis of a solar-driven CaL plant for TCES using two different life cycle assessment methodologies: GREENSCOPE [4] and SimaPro [5]. To this end, various alternatives at several stages of the project design phase were analysed. This analysis investigates and classifies the proposals for future process improvements, providing a classification based on sustainability for the decision makers, allowing them to set the route for a sustainable development of the process.

Three process alternatives for the CaLTCES process are presented: V_0 - Use of CO_2 as fluidization fluid and 100 % purge of limestone; V_1 - Use of steam as fluidization fluid; and V_2 - Use of steam as fluidization fluid at a lower temperature (800 ºC) in the calciner. When no CO_2 is present in the fluidization stream, the calcination reaction is favoured, and a lower temperature may be used in the reactor, resulting in a more sustainable process, as corroborated by the results (Figure 1).

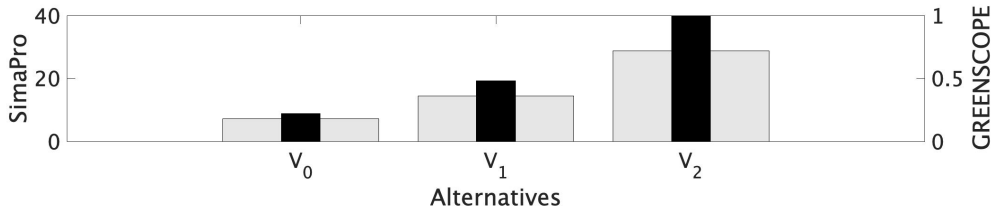

Figure 1. CaLTCES plant analysis results from SimaPro single score (grey bars) and GREENSCOPE (black bars).

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. All the authors acknowledge the financial support received from FCT through project PTDC/EAM-PEC/32342/2017.

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O20

Sodium Salt with Fatty Acids Eutectic mixtures as Electrolytes for Supercapacitors

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The world's energy demand is increasing as a consequence of a growing and highly technological population that highly relies on fossil fuels. Therefore, engaging renewable energy in the energy world supply is highly requirable. However, since most of renewable energy are intrinsically intermittent, energy harvest and distribution will largely depend on energy storage devices, namely supercapacitors1. Moreover, the commercially available SCs essentially depend on organic electrolytes to reach wider potential windows[1]. These electrolytes have a high environmental impact and typically have concerning levels of toxicity and are also flammable leading to safety risks. For this reason, it is desirable that the materials used to develop these devices are not only high-performance but also the most environmentally friendly possible[2].

In this work, mixtures of water with eutectic systems of sodium hexanoate with different carboxyl acids (hexanoic acid, octanoic acid, nonanoic acid and decanoic acid) are studied as potential electrolytes for Electrical Double Layer Supercapacitors (EDLCs).

In the first part of this study, physical characterization of these mixtures is studied through measurement and exploration of several properties, namely the conductivity, viscosity and density. In the second part, the electrochemical performance of these mixtures is tested in EDLC cells with carbon-based material electrodes through Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD).

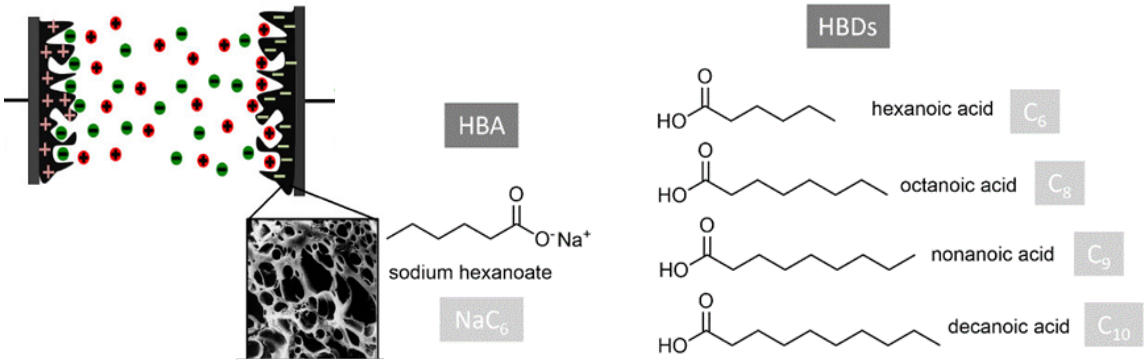

Figure 1. DES used to prepare the electrolyte for EDLC Supercapacitors.

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O21

Continuous-Flow Electrochemical Oxidation of Abietanes

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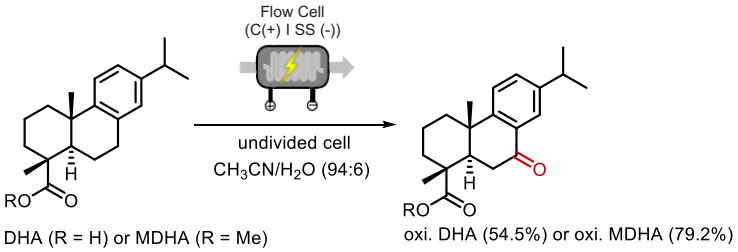
Rosin or Colophony is a natural resin that is extracted from pine trees. Besides having multiple industrial applications, it is also constituted by a group of diterpenes known as abietanes, which, along with its derivatives, has been found to have a wide variety of interesting biological activities, including antimicrobial, antiviral, antitumoral, and anti-inflammatory. [1,2]

The benzylic oxidation of dehydroabietic acid, and its methyl ester derivative has been previously reported using various oxidative protocols, such as Swern oxidation [3] or using Chromium trioxide in either stoichiometric [4] or catalytic quantities.[5,6] However, these protocols fail in the context of sustainability for several reasons, such as the use of toxic reagents and stoichiometric amounts.

Herein we present a sustainable protocol for the oxidation of both dehydroabietic acid and abietic acid, and their methyl ester derivatives. We used modern electrochemical methods to achieve good yields of the ketone for both abietanes. Furthermore, we report the development of an electrochemical flow process towards increase its productivity. [7-9] Finally, we extended this strategy to colophony and report its successful application both in batch and flow (https://chemrxiv.org/engage/chemrxiv/article-details/624ab0cb8048825467032beb).



Scheme 1: Continuous Flow Electrochemical Oxidation of Dehydroabietic Acid (DHA) and its Methyl Ester derivative (MDHA).

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O22

The unexpected reactivity of Ruthenium hydrides supported by di-tert-butylpyridylphosphine

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Metal hydrides are an important class of compounds. Industrially relevant processes like hydrogenation, hydrosilylation and hydroformylation are catalyzed by transition metal hydrides, that are also intermediates in other important reactions like C-H activation and olefin isomerization. More recent applications can be found in emerging fields like Energy Conversion and Hydrogen Storage, where they provide H^- for generation of H_2, and materials that can reversibly and heterolytically cleave H_2, respectively.[1]

The reactivity of ruthenium hydride complexes that are supported by 2-((ditert-butylphosphino)methyl)pyridine, **L1**, and 2-[bis(2-methyl-2-propanyl)phosphino]pyridine, **L2**, was explored (Figure 1).[2] $\{Ru(COD)Cl_2\}_n$ reacts with **L1** at 80 °C in the presence of a base and 10 bar of H_2 to afford the expected [Ru(**L1**)$_2$(H)Cl], **1**, but the same reaction with **L2** gave unexpectedly the complex [Ru(**L2**)(P(H)^{t}Bu$_2$)(H)Cl], **2**, that results from the cleavage+H2 addition to a P-C bond. We were able to establish that under the chosen reaction conditions the first species formed is [Ru(**L2**)$_2$(H)Cl], **3**, and that this species decomposes to give complex **2** and is in equilibrium with [Ru(L2)2Cl2], **4**. The proposed mechanism obtained by DFT has the protonation of the carbon as the highest energy step (38.9 kcal/mol), consistent with a slow reaction. Preliminary catalytic results for the hydrogenation of benzaldehyde are also reported.

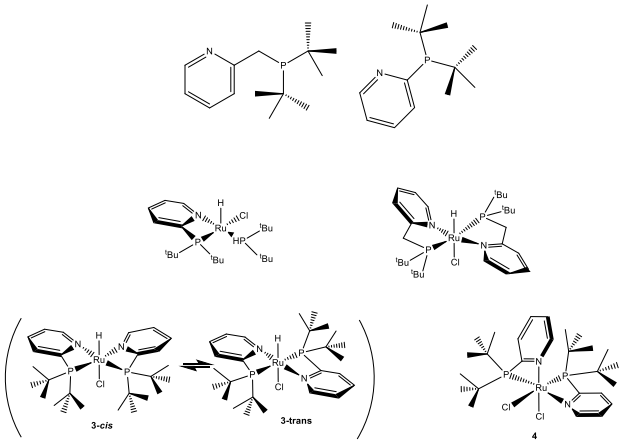

Figure 1. Ligands and ruthenium complexes

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects **UIDB/00100/2020** and **UIDP/00100/2020**. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project **LA/P/0056/2020**. V.R.G.C acknowledges FCT for the doctoral fellowship **PD/BD/147841/2019** integrated in the PhD Program in NMR applied to chemistry, materials, and biosciences (**PD/00065/2013**). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by **Infrastructure Project No 022161** (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).

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O23

Peroxidative oxidation of cyclohexane in aqueous CH_3CN medium using Cu(II or I) complexes bearing hydrazone or 1,3,5-triaza-7-phosphaadamantane-derived ligands

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The mild peroxidative oxidation of cyclohexane by H_2O_2, yielding a mixture of cyclohexanol and cyclohexanone (KA oil), was performed under conventional heating but also employing non-conventional conditions, such as the use of microwave (MW) irradiation or a supercritical carbon dioxide ($scCO_2$) medium, a "green solvent" that possesses moderate critical pressure and temperature (p = 73.8 bar and t = 31.1 ˚C) and may be easily separated from the catalytic system by a simple depressurization [1].

Two tetranuclear Cu(II) complexes from arylhydrazones of malononitrile (compounds **1-2**) and a mononuclear Cu(I) compound bearing a functionalized 1,3,5-triaza-7-phosphaadamantane (PTA) ligand, $[CuCl_2(PTA\text{-}CH_2\text{-}C_6H_3\text{-}p\text{-}OH\text{-}m\text{-}CHO)_2]I$ (complex **3**), exhibited an interesting catalytic activity towards the formation of KA oil in a homogeneous acetonitrile/water medium.

Regarding the cupric compounds, the best results were attained in the presence of pyrazine-2-carboxylic acid (PCA) with **1** and **2** (26% and 24% yield; TON = 52.0 and 48.0, respectively). In a CH_3CN–$scCO_2$ medium, with HNO_3 as acid promoter, only 17% yield was achieved using **1** as catalyst, and 21% when employing **2**. Total yields of oxygenates up to 14 (with **1**) and 13% (**2**) and TOFs of 56.0 and 52.0 h^{-1}, respectively, were obtained under MW irradiation [2].

From the new Cu(I) complexes with N-alkylated PTA derivatives, compound **3** displayed the highest catalytic activity, affording up to 21% of cyclohexanol + cyclohexanone using 0.1 mol% of the catalyst (TON = 42.0); under MW irradiation, 18% yield of KA oil was obtained (TON = 36.0 and TOF = 24.0 h^{-1}) using a similar catalyst loading [3].

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O24

Study of new Ni-based coordination polymers as promising De-NO_x photocatalysts

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Currently there is a great concern to address the pollution by NO_x gases (NO + NO_2) because of their hazardous effects on human health and environment. The concentration of these gases in the air of cities (ppb levels) can be directly reduced through photocatalytic technology (De-NO_x process), namely by using the sunlight irradiation and a photocatalyst under mild conditions. Nevertheless, this technology is not extended enough mainly because the commercial photocatalysts (TiO_2-based) are active only under UV light, thus not taking an advantage of the visible light (~43% of the received solar energy) and resulting in low NO_x removal efficiencies [1]. Hence, there is a high demand toward the design and development of alternative and more efficient De-NO_x photocatalysts.

Coordination polymers (CPs) have been reported as emerging candidates for many photocatalytic applications [2], owing to their structural variability, controllable pore size, high dispersion of active sites, and potential charge transfer. In particular, nickel centers are quite interesting for building functional CPs by coordination with nitrogen/oxygen-containing ligands, since Ni can show variable oxidation states, diverse geometries and ligand field effects [3]. Additionally, nickel is an earth-abundant metal and may extend the visible-light response in CPs due to its *d-d* electronic transitions. On the other hand, aromatic ligands can improve an absorption range of light and facilitate the crystallization of CPs.

The primary aim of our project is to generate new Ni-CPs by carefully modifying the self-assembly synthesis in a system comprising of Ni^{2+} precursor and a range of aromatic carboxylic acid linkers. The ligands that are being currently explored include 5-hydroxyisophthalic, 5-nitroisophthalic, 2,6-naphthalenedicarboxylic, 4,4′-oxybis(benzoic acid), 5-sulfoisophthalic acid, and 4-sulfophthalic acids, which are commercially available and of relatively low cost. Besides, the presence of variable number of aromatic rings and carboxylic acid groups can lead to the assembly of structurally and topologically different architectures, which can influence the absorption of light and photocharge transfer. These factors may help to optimize the most appropriate Ni-CPs for the photocatalytic De-NO_x reaction. This communication will discuss our ongoing studies and preliminary results on the synthesis, structural characterization, and photocatalytic application of the obtained CPs and derived materials.

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O25

Synthesis of novel D-glucopyranuronamide-based nucleoside analogs of potential anticancer interest

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The synthesis of D-glucuronamide-containing molecules has attracted increasing attention in the context of the search for new bioactive compounds, which is motivated by the biological profile reported for either natural or synthetic derivatives containing this saccharidic unit.[1]

Moreover, the synthesis of D-glucuronamide derivatives offers opportunities for performing structural variations in a regioselective manner at C-6 on a *gluco*-configured template by varying the N-substitution, which enables bioactivity tuning. Anomeric functionalization of N-substituted D-glucuronamides can also be easily achieved using common methods in carbohydrate chemistry.

Within our continuous interest in the synthesis of new potentially bioactive D-glucuronamide-based compounds, and motivated by our previous reports showing the anticancer potential of *N*-dodecyl glucuronamide-based nucleosides,[2,3] in this communication we report on the synthesis of novel D-glucopyranuronamide-derived nucleosides containing *N*-propargyl or *N*-dodecyl substituents and a *N*-linked nitrogeneous heteroaromatic moiety at C-1, namely a purine, pyrimidine or a 1,2,3-triazole unit. The synthesized molecules included [*N*-(glucuronamidyl)triazolyl]methyl phosphonates as potential sugar diphosphate mimetics, glucuronamide-based (purinyl)methyl triazole nucleosides or related purine or uracil nucleosides. For their access, D-glucofuranuronolactone was used as starting material and key synthetic steps included amidation, furanose to pyranose isomerization, anomeric azidation, azide-alkyne 1,3-dipolar cycloaddition, Arbuzov reaction or N-glycosylation.

Antiproliferative evaluation revealed significant activities of some nucleosides against breast cancer and leukemia cell lines, in some cases with a GI_{50} value close to that of a clinically-used drug.

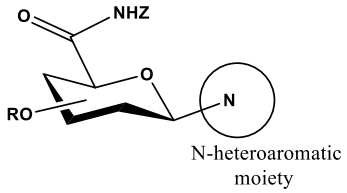

Figure 1 *- General structures of the synthesized nucleosides*

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O26

Exploring the anticancer potential of novel Cu(II) and Zn(II) complexes of 8-hydroxyquinoline Schiff bases

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Cancer continues to be a major public health problem despite recent progress in treatment and prevention. Many cancers still lack effective therapy, and the development of acquired resistance to cytotoxic agents is a growing concern. To tackle this issue and create novel, effective, and selective anticancer drugs, our group has developed new families of metallodrugs based on ligands derived from 8-hydroxyquinoline (8HQ)[1-3], a scaffold that has demonstrated great potential in cancer treatment. Our approach involves combining a bioactive ligand (8-HQs substituted at position-2 with piperidine/morpholine type moieties) with a therapeutic metal ion, Cu(II) or Zn(II), within the same molecule, to achieve additive and/or synergistic effects. The newly synthesized compounds were characterized by elemental analysis, ESI mass spectrometry, FTIR, NMR or EPR and UV-Vis absorption spectroscopies, as well as by single-crystal X-ray diffraction, which helped elucidate their chemical structure in solid state and solution. All complexes were tested for their aqueous stability and interaction with biologically relevant molecules, namely BSA (bovine serum albumin), through fluorescence quenching experiments and/or circular dichroism. All complexes are able to bind this protein, although several hours are needed to reach equilibrium. The pKa values of the ligands and formation constants of the complexes were determined by spectrophotometric titrations, showing higher stability for the Cu(II)-complexes. The antiproliferative activity of the ligands and complexes was evaluated in a human (A375) and murine (B16F10) melanoma cell line and in a non-cancerous keratinocyte cell line (HaCaT), to assess selectivity. Overall, results indicated that complexation had a positive impact on the cytotoxicity, with the Cu(II)-complexes being the most potent among all tested compounds, although higher selectivity is required. The lead Cu(II)-complex was encapsulated in liposomes to improve water solubility and enhance its efficacy and selectivity towards melanoma cells.

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O27

Determination of six PEth homologues in whole blood by liquid-liquid extraction and UHPLC-MS/MS

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Phosphatidylethanol (PEth) is a specific direct alcohol biomarker, with a half-life in blood of approximately 4 days but in some cases up to 12 days, significantly longer than other alcohol biomarkers, such as ethanol (figure 1) [1,2]. The consumption of alcohol is correlated to the blood concentration of PEth and can be used to distinguish different drinking patterns, such as heavy- and social drinking [3,4]. In this study, we developed an ultra-high performance liquid chromatography – tandem mass-spectrometer (UHPLC-MS/MS) method for the quantitative determination of six PEth homologues in whole blood, using previous findings from how to avoid co-elution of PEth and unwanted phospholipids [5]. Chromatographic separation was performed on an C18 column with a mobile phase consisting of 0.025% ammonia aqueous solution and methanol was used. Whole blood samples were prepared by liquid-liquid extraction. The developed UHPLC-MS/MS method for the determination of six PEth homologues was fully validated in whole blood. Each PEth homologues has its own deuterated internal standard, except PEth 18:1/18:1. Inter-assay precision and accuracy were within ≤ 18% and ≤ 14%, respectively. The extraction recoveries obtained were within 37-51% and no matrix effects were observed for all PEth homologues. The validation showed that UHPLC-MS/MS method is precise, accurate, and sensitive for its purposes and it's a robust and sensitive bioanalytical method for the determinations of the six PEth homologues in whole blood.

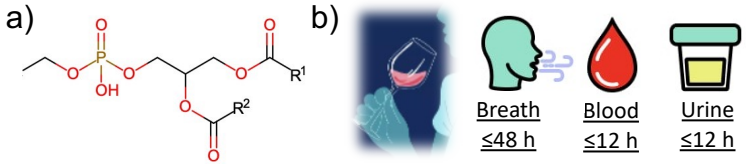

Figure 1 - Chemical structure of PEth homologues (a) and ethanol detection time (b).

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O28

Targeting PBP2a to overcome β-lactam resistance in methicillin-resistant *Staphylococcus aureus*

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The multi-resistance of methicillin-resistant *Staphylococcus aureus* (MRSA) to β-lactams is a worldwide cause of nosocomial infections with a high mortality rate. This resistance comes from the *mecA*-coded PBP2a protein (Figure 1), with low affinity towards β-lactams antibiotics [1, 2]. Reduced susceptibility to β-lactams is related to PBP2a changes in the catalytic residue Ser403, to the presence of allosterically-controlled active site-protecting loops and to the gatekeeping residues Met641 and Tyr446 that prevent β-lactams from accessing the active site [2]. Thus, innovative antibiotics that circumvent these protections are required.

In this work, a structure-based computational molecular docking screening approach was employed with Autodock Vina, using the X-ray structures of both closed and open PBP2a conformations (PDB ID 1vqq and 3zg0, respectively). Various lactam scaffolds, fluorenone, flavone and quinazolinone derivatives were tested as possible inhibitors for both sites. Known specific inhibitors were also tested. Molecular dynamics simulations using GROMACS were deployed to understand whether binding of natural substrate and hit compounds can induce protein conformational changes.

The known inhibitor L-695256 showed best results to the target protein, with affinities of -6.2 kcal/mol (allosteric site, native PBP2a) and -9.4 kcal/mol (active site, open PBP2a). Hit compounds identified in this work presented significant improvements in affinity for both catalytic sites, for instance, -8.1 kcal/mol towards the allosteric site and -12.1 kcal/mol towards the active site. Hit compounds also recapitulate the protein-ligand interactions of known inhibitors. Moreover, binding of natural substrate in the allosteric site leads to an increase in the RMSD of the loops protecting the active site, suggesting that conformational changes are occurring near the catalytic residue. Upon allosteric binding of the natural substrate, the distance between the catalytic Ser403 and gatekeeping Tyr446 residues increases, suggesting that catalytic site is more exposed. This is observed also when selected hit compounds are bound at the allosteric site.

Results indicate that tested compounds are promising hits targeting PBP2a, and MD simulations will soon enable us to understand how binding to the allosteric site will allow binding of the same molecule in the active site.

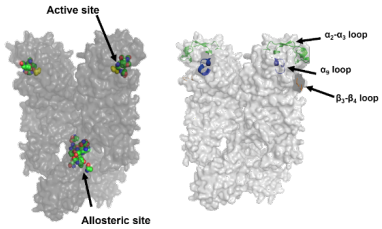

Figure 1. Overall structure of the PBP2a protein.

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O29

Exploring the Temperature Effect on Potentiostatically Synthesized PEDOT:PSS films: Electrochemical and Mass Flow Characterization

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Poly (3,4-ethylenedioxythiophene) (PEDOT) is an Electronically Conducting Polymer (ECP) that owns physical and chemical properties [1-2] favourable to its use in energy storage. As a consequence of the low solubility of its monomer in aqueous solutions, poly (sodium-4-styrenesulfonate) needs to be used in the polymerization process, allowing the formation of a stable dispersion of the monomer. This polyanion does not contribute to charge transport since the anionic charges are immobilized in the bulk of the polymeric matrix being counterbalanced by electrolyte cations. The sulfonate groups also concede a charge compensation to counteract the positive charges of oxidized PEDOT thiophene rings [3]. Therefore, during the film redox conversion, there will be cations movement from the polymer to the solution in oxidation and the opposite will occur during the film reduction. This phenomenon is known as pseudocationic doping and is the desired process for the application of these materials as cathodes for sodium-ion batteries. The synthesis temperature may have an effect not only on the polymerization kinetics, as well as on the morphological and mechanical properties of the PEDOT:PSS [4].

In this work, PEDOT:PSS films were potentiostatically synthesized at 0 and 40 ºC on platinum electrodes from aqueous solutions containing the monomer and the polyanion. The electroactivity of these films was evaluated at room temperature by cyclic voltammetry in acetonitrile solution containing $NaClO_4$. The mass transfer phenomena, taking place during the redox conversion of PEDOT:PSS films, deposited at different temperatures and with different thicknesses, were investigated by coupling the electrochemical methods with microgravimetry (EQCM) and Probe Beam Deflection (PBD). Both techniques are well-suited for measuring the mass transport, since they transduce the ionic flows that occur during the redox conversion of the polymeric matrices, while solvent molecules involved in mechanical adjustments are only probed by EQCM. To evaluate the optical properties and morphology of the synthesized films, ellipsometry and Atomic Force Microscopy (AFM) were also employed.

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O30

Stimuli-Triggered Activated Nanoparticles to Eliminate Formaldehyde Emission

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Food and Agriculture Organization of the United Nations (FAO) reported that in 2018, the global wood-based panel production reached 408 million cubic meters, with an estimated value of over 200 billion USD.[1] Due to their properties, urea-formaldehyde resins (UFRs) are the most used in wood composites, such as wood-based panels, with this market alone accounting for 95% of total consumption of UFRs. Despite their wide utilization, UFRs present a major handicap: the formaldehyde emission during panel manufacture and service life. The regulations concerning this carcinogenic agent have become more stringent with time, and the expectation and the new and more strict ones will be imposed in the near future.[2,3]

Several strategies have been tested to decrease formaldehyde emission in cured resins. The reduction of the formaldehyde/urea ratio have shown low efficiency, since lowering free formaldehyde content and emission would impair the resin cure and its final performance. On the other hand, the use of formaldehyde scavengers provided mixed results: while some do not show any improvement, the promising ones hinder the physical properties of the panels.

The goal of this project is to develop a new platform to drastically decrease formaldehyde emissions in UFR wood panel applications, while maintaining/improving the of the final products. We synthesized polymer core-shell nanoparticles featuring a polystyrene sulfonate (PSS)-rich (core) and a polystyrene (PS)-rich (shell) (Figure 1). The particles feature a temperature-triggered activation mechanism that promotes the curing of UFRs only during the production of the wood-based composites. During the hot-press treatment, the temperature rises to the region of polystyrene's T_g. Due to the "softening" of the PS chains, the sulfonate groups interact with the aqueous dispersion and react with the free formaldehyde present to lower the pH and induce the cure of the resin.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. PhD scholarship SFRH/BD/145416/2019 funded by Fundação para a Ciência e Tecnologia.

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O31

Thermodynamic and Kinetic approach of the Formation of Multicomponent-Crystals with Different Stoichiometries: Maleic Acid and Phenylalanine

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Co-crystallization (the formation of crystals containing two or more distinct molecules in the crystal lattice) has been attracting significant interest in recent years as a strategy to improve the physical properties of organic materials without compromising their function. A widely used synthesis route to obtain these materials is through mechanochemistry, which uses mechanical energy to promote the combination of two or more solid precursors in a single crystal lattice. Little is known, however, about the energetics and, particularly, the kinetic/mechanistic aspects involved in this method. Recent advances in the use of synchrotron X-ray diffraction started to allow for a real-time in situ study of this process [1]. Here we describe, for the first time, the study of the kinetics and mechanistic aspects of the formation of cocrystals of maleic acid with phenylalanine with different stoichiometric based on synchrotron X-ray diffraction data.

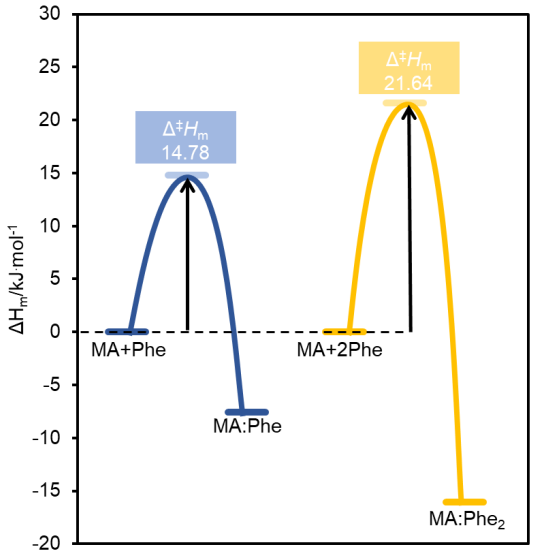

Figure 1. Enthalpy profile for the reaction of formation of MA:Phe (blue) and MA:Phe$_2$ (yellow).

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This research was also supported by the FCT-DAAD program for cooperation in science. A doctoral grant awarded by the FCT to I. Feliciano (2021.04637.BD) is also gratefully acknowledged.

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O32

Studying shifts in the magnetic behaviour of iron complexes via ligand and counterion modifications

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The spin crossover effect has been widely studied in several areas of chemistry, especially when correlated with Fe(II) and Fe(III) species, with a significant impact upon the transition between energy states in this type of complexes, for example [1]. Complementary studies suggested that potential modifications of the ligands or the anionic counter ion in these complexes – one case being the presence of halogen atoms in the structure of N-(ethyl)-N-ethylenediamine salicylaldehyde (SalEen) – affect the pattern of the magnetic profile obtained for these Fe(III) species [2]. Also, the type of solvent used in these experiments can interfere with the type of species obtained, even going as far as producing distinct polymorphs within the same system [3,4]. With this in mind, we focus on the optimization of previously studied Fe(III) complexes and the synthesis of newer ones, to extend the library of species under study – while also trying to obtain differing species, by varying the solvent of the crystallisation process.

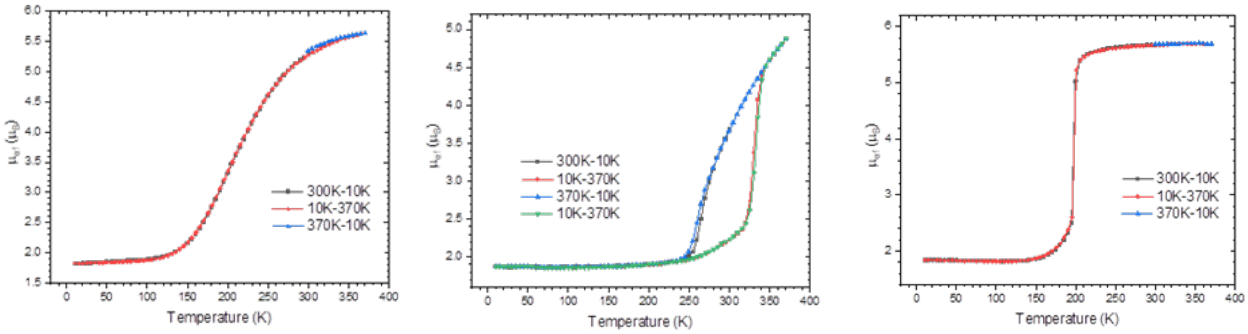

Figure 1. Magnetic profiles for a set of $[Fe^{III}(X\text{-SalEen})]ClO_4$ complexes (X=H, Br and Cl).

Acknowledgments: We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021. Centro de Química Estrutural (CQE) and Institute of Molecular Sciences (IMS) acknowledge the financial support of Fundação para a Ciência e Tecnologia (Projects UIDB/00100/2020, UIDP/00100/2020, and LA/P/0056/2020, respectively). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).
P.N.M. acknowledges FTC for financial support (CEECIND/00509/2017).

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Abstracts
CQE |
Infrastructure & Facilities

IF1

CQE-Ciências: Lab & Computer Infrastructures facility

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The Lab and Computer Infrastructures facility of the Centro de Química Estrutural (CQE) available at the Faculty of Sciences of the University of Lisbon (FCUL), was recently created and integrates multiple scientific research laboratories whose instrumental infrastructures are now available to provide research support services beyond the CQE / FCUL universe.

This organizational structure has the objective of making these research support resources more operational and available to the entire scientific community, *e.g.*, public laboratories, private companies, startups, etc.

The Lab and Computer Infrastructures facility at CQE-Ciências involves 8 multidisciplinary infrastructures, organized in 14 laboratories making more than 50 different equipments available to anyone interested, starting by the CQE scientific community.

The Atomic Force Microscopy (AFM) and the Cell Culture and Flow Cytometry (BSL-2) Infrastructures are the two facilities already accessible, Figure 1. Detailed information about them can be found on the infrastructures' website where each set of equipment can be booked by request on a simple and users-friendly online booking platform which will de duly presented in this communication.

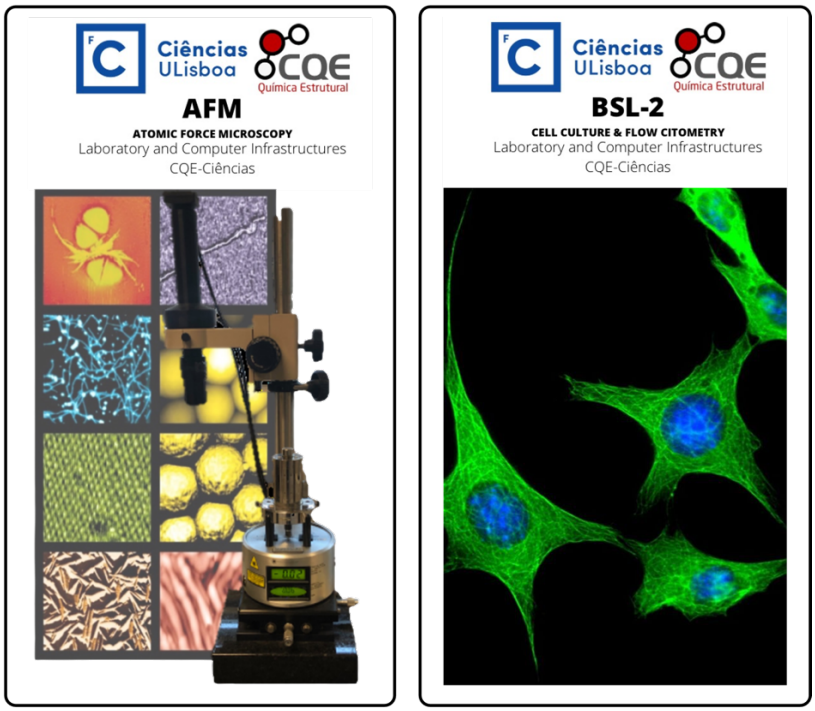

Figure 1. Atomic Force Microscopy (AFM) and Cell Culture and Flow Cytometry (BSL-2) Infrastructures.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

IF2

biobank|CQE: a powerful tool for medicinal chemistry

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Biobanks are crucial tools for translational research. The biobank|CQE has been created to support the development and testing of new molecules with possible health benefits, and as a repository of human and non-human samples relevant to the Centre's research.

Currently, the biobank|CQE gathers a collection of human specimens, ranging from blood samples and isolated blood cells, to preserved tissues and subcellular fractions, as well as animal tissues.

Human samples have been used to develop cellular models in order to study the effects of commercial drugs on the activity of immune cells. This approach relies on the isolation of immune cells from healthy donors, exposure of those cells to specific drugs and the identification of altered pathways resorting to MS-based techniques.

As the biobank|CQE also collects samples from medicated donors, the previously identified altered pathways are also being identified in blood samples of such donors and correlated with their medication. This double-edge approach allows for the quick and simple identification of possible drug-side effects that can be used in drug repurposing approaches.

On the other hand, the resources of the biobank|CQE allow the rapid screening of numerous molecules to probe their toxicity or biological activity, in different cellular targets.

An overview of the different resources and their application to study molecules as possible new drugs will be given.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

IF3

NMR: a support technique at CQE

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The NMR facility at CQE is part of the IST-node of the Portuguese NMR Network (PTNMR). Its main mission is to support researchers in chemistry and related areas by providing hands-on training in NMR and access to NMR machines. The facility is currently equipped with four NMR machines: a 300 and a 400 MHz, open to all users, a 500 MHz equipped with eight different probeheads and a 300 MHz dedicated to solid-state NMR.

The NMR facility has recently acquired several pieces of equipment that increase the number of experiments the facility has to offer its users. These include a 4 mm solid-state NMR probehead for the 500 MHz machine, a 7 mm solid-state NMR probehead (WB) for the 300 MHz ss NMR machine, a broad band diffusion NMR probehead for the 500 MHz machine and a high-pressure NMR cell (for pressures up to 1 kbar). A new online booking system was also implemented.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project No 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).

IF4

Mass Spectrometry Facility at Instituto Superior Técnico

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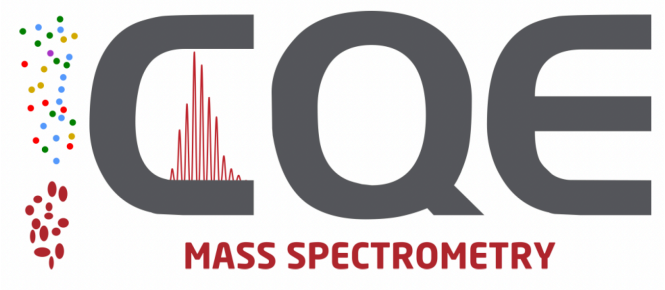
The Mass Spectrometry (MS) Facility at IST encompasses the MS labs coordinated by CQE researchers. These laboratories are involved in numerous R&D projects and deliver a variety of services in the various fields of chemistry.

Elemental, isotopic and structural analysis allows the determination of accurate masses, molecular formulas and structures, and characterization of novel chemical entities, and assists in the characterization and quantification of natural products and in residue analysis. The application of MS to organic and inorganic chemistry areas offers the possibility to investigate the intrinsic reactivity and the associated thermochemical and kinetics parameters of metallic species, including of medium and long half-life radionuclides, at a molecular level. Untargeted approaches, coupled with targeted quantitative approaches, allow screening, prioritizing, and identifying the environmental occurrence and exposure to toxic and genotoxic agents.

Complete processing workflows, going from sample to bioinformatics-driven data analysis, allow the metabolomic, proteomic and lipidomic profiling of biological fluids, tissues, cells, and many other sample types, assisting the biological chemistry research areas of CQE, with a strong component of toxicology screening, at both the chemical and biological levels.

As a whole, the Mass Spectrometry Facility at Técnico offers the tools and know-how required to potentiate R&D impact at both the academic and societal levels, contributing to all the Thematic Lines of CQE.



Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. The Mass Spectrometry Facility is part of the Portuguese Mass Spectrometry Network (Rede Nacional de Espectrometria de Massa, ref. LISBOA-01-0145-FEDER-022125)

Abstracts
Poster Presentations

P1

Functionalization of Natural Bisquinolizidine Alkaloids

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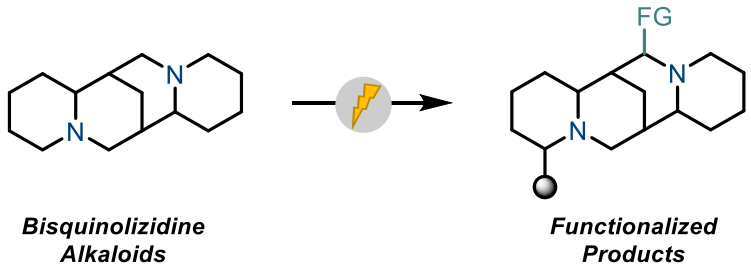
Bisquinolizidine alkaloids (BQA) are found in several plants of the subfamily *Faboideae*. Structurally, they contain a chiral bispidine core decorated with fused N-annulated piperidinone or piperidine moieties [1]. An important member of the group is sparteine, which is commonly used as a chiral ligand for various metals in asymmetric synthesis [2]. However, the limited reactive functional groups on sparteine and other BQA pose a functionalization challenge. Thus, limiting their use in metal-free organocatalysis. Taking advantage of the recent advances in electrochemical organic synthesis that enables gram scale reactions, a site-selective electrochemical C-H activation was explored, and several functional group transformations are currently being investigated (**Scheme 1**) [3].



Scheme 1: Electrochemical functionalization of bisquinolizidine alkaloids

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We thank the FCT for financial support (UIDB/04138/2020, UIDP/04138/2020, and project PTDC/QUI-QOR/1786/2021). JASC thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND

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P2

Green metrics for the production of methanol

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The purpose of this work is to analyse different reactions that have in common the production of methanol in different ways with different catalysts.

Moreover, methanol is a promising energy carrier because, as a liquid, it is easier to store than hydrogen. It can also be used directly as fuel in combustion engines, or as a solvent or as an antifreeze in pipelines.

Its producing carries a massive impact on the environment. It is for this reason that the aim of this project is to look for the most efficient and less harmful process for the environment.

Therefore, several reactions have been analysed in order to calculate different parameters that define the level of greenness of the reaction. There are two different types of parameters: one relates with general greenness parameters, such as the *E* factor and others are defined by the twelve principles of chemistry.

The implications in several industries, such as automotive, aerospace, and naval[1], makes this topic relevant in several fields.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P3

HBpin/$MoO_2Cl_2(H_2O)_2$ as an efficient catalytic system for the reduction of esters, lactones and polyester plastic waste

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The huge amount of plastic waste produced every year is causing serious environmental problems to the planet. It is extremely urgent to develop new methodologies to convert plastic waste into value-added products, contributing to the circular economy.

In the recent years, several methodologies have been developed for the depolymerization of plastic waste. Among them, reductive depolymerization proved to be an effective protocol to convert plastic waste into valuable compounds and raw materials for industry.[1]

In continuation of our work,[2-4] in this communication we report a very efficient protocol for the reductive depolymerization of various polyester plastic waste with the catalytic system HBpin/$MoO_2Cl_2(H_2O)_2$, under mild reaction conditions, with excellent yields (Fig. 1). This methodology was also successfully applied to the reduction of esters and lactones (Fig. 1).[5]

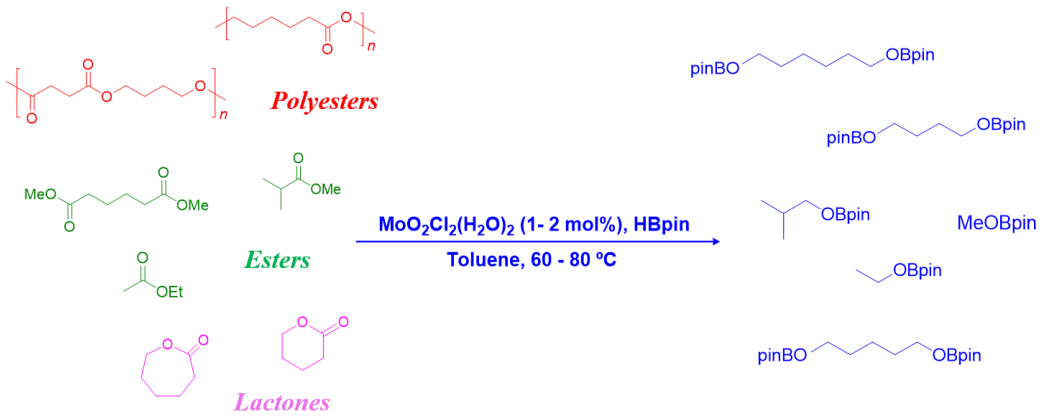

Figure 1. Reduction of polyesters, esters and lactones with the catalytic system $MoO_2Cl_2(H_2O)_2$/HBpin.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This research was supported by FCT through project PTDC/QUI-QOR/0490/2020. DLL thanks to FCT for the grant.

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[1] Fernandes, A. C.; *Green Chem*. **2021**, ***23,*** 7330-7360.
[2] Nunes, B. F. S., Oliveira, M. C., Fernandes, A. C.; *Green Chem.* **2020**, 22, 2419-2425.
[3] Fernandes, A. C.; *ChemSusChem* **2021**, *14*, 4228-4233.
[4] Lourenço, D. L., Fernandes, A. C.; *Catalysts* 2022, *12,* 381.
[5] Lourenço, D. L., Fernandes, A. C.; *Molecular Catal. 2023, 542, 113128.*

P4

Valorization of polyester and polycarbonate plastic waste catalyzed by zinc compounds

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Plastics make our lives much more convenient. The excellent properties of plastics in terms of low cost of manufacturing, light weight and durability have enhanced their applications and led to a displacement of traditional materials, such as wood, metals and ceramics. As a result, society has become completely dependent on plastic. In parallel with the consumer behavior change / awareness raised behavior regarding the use of plastic, it is also urgent to develop new methodologies for the valorization of plastic waste into value-added compounds.

In continuation of our work,[1-4] in this communication we describe a novel methodology for the reductive depolymerization of plastic waste using zinc catalysts. This method was successfully applied to the depolymerization of a variety of polyester and polycarbonate waste with excellent yields under mild reaction conditions.

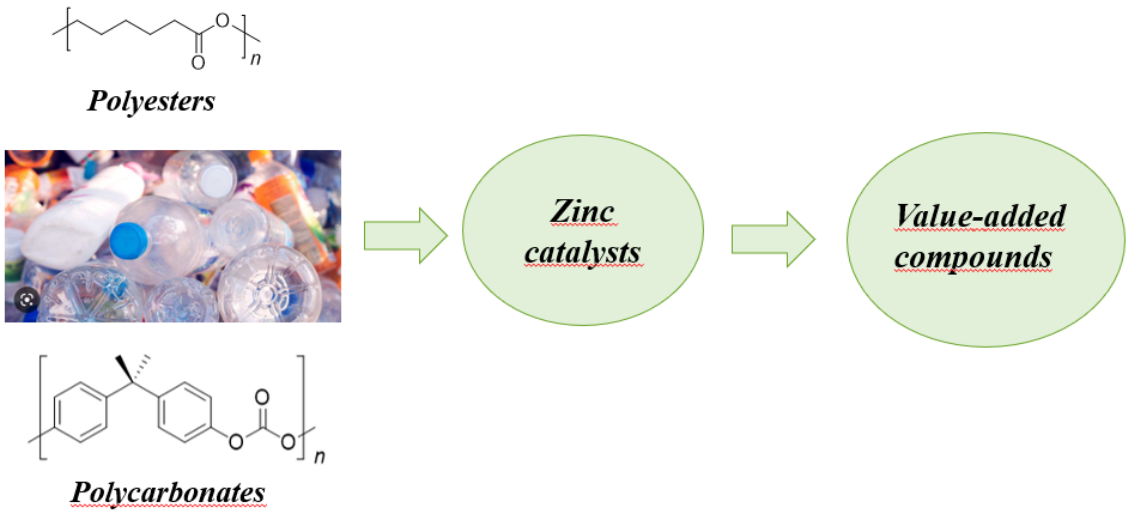

Figure 1 – Valorization of polyester and polycarbonate catalyzed by zinc compounds.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This research was supported by FCT through project PTDC/QUI-QOR/0490/2020.

References:

[1] Nunes, B. F. S., Oliveira, M. C., Fernandes, A. C.; *Green Chem.* **2020**, 22, 2419-2425.
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[4] Lourenço, D. L., Fernandes, A. C.; *Molecular Catal. 2023, 542, 113128.*

P5

Enantioselective Epoxidation of Styrene Derivatives with Fe_3O_4 Magnetic Nanoparticles Functionalized with Mo

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Epoxides are an important group in modern chemistry since they can be extremely valuable as intermediates in reactions in the fine chemicals and pharmaceuticals industry. The easiest and most efficient way to synthesize these compounds is through the epoxidation of the corresponding olefin in the presence of an oxidant. [1, 2]

In the present work, styrene, *trans*-β-methylstyrene and 4-chlorostyrene were the chosen olefins to study the epoxidation reaction using iron oxide magnetic nanoparticles as their catalyst.

Iron oxide magnetic nanoparticles are a heterogeneous catalyst which provides the advantage of being easily removed from the reaction through filtration when compared to homogeneous catalysts. However, the heterogeneous catalysts are usually not as active and selective as the homogeneous ones and that's where the nanoparticles come in. Due to their nanosize, their superficial area is bigger and, consequently, so is their activity.

The magnetic nanoparticles were prepared by a co-precipitation method using Fe(II) and Fe(III), followed by a silica coating which offered stabilization to the core and the possibility to graft a pyridine derivative ligand. To functionalize the surface, a $[MoI_2(CO)_3]$ complex was then coordinated. The success of these 4 steps was confirmed by SEM and TEM analysis, FTIR spectroscopy and powder XRD.

The catalytic tests were performed at 328 K and 353 K using TBHP and H_2O_2 as oxidants and CH_2Cl_2, CH_3CN, EtOH and toluene as solvents. The obtained results were very promising, showing higher conversion values when TBHP was the oxidant and with a temperature of 353 K. The iron oxide magnetic nanoparticles also proved to be a more efficient catalyst for the epoxidation of *trans*-β-methylstyrene.

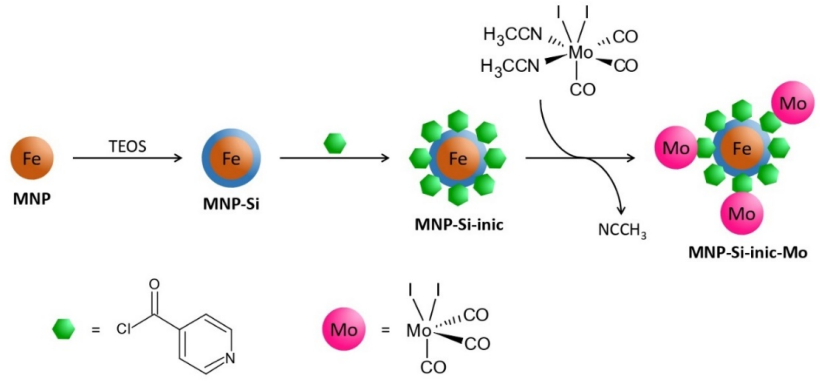

Figure 1. Synthetic pathway adopted to prepare the magnetic iron oxide nanoparticles.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P6

Synthesis of ultra-high molecular weight polyethylenes catalyzed by vanadium aroylhydrazine-arylolates

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Synthetic polymers play important roles in our daily life due to their good properties and easy preparation. Polyethylene materials account for a significant share of the polymer market, with production estimated at 120 million tons per year. Applications range from packaging, water and gas pipelines, car parts, toys, furniture, medical devices to building materials and so-forth. They are also irreplaceable as copolymers for the synthetic rubber and elastomer manufacturing industries, even for the manufacture of photovoltaic films or artificial lungs, and in the production of cyclic olefin copolymers [1]. Research into the development of new catalysts remains an important topic, since they control the final polymer morphology, which can be of interest with the growing demands for the production of new specialized polymers and could also help to improve the performance of the existing ones, manufacturing processes and technologies, and costs [2]. Vanadium catalysts have played important roles [3]. We prepared a series of vanadium(V) aroylhydrazine-arylolates and employed them in ethylene polymerization to produce ultra-high molecular weight polyethylene (UHMWPE) [4]. MAO or DMAC could activate the complexes **V1–V3** to catalyze the polymerization reaction with an activity up to 3.37 × 10^6 g mol^{-1} h^{-1} at 60 °C. The polyethylene obtained has a molecular weight around 3 million g mol^{-1}, being the highest molecular weight achieved by a vanadium catalyst of this type so far. The cocatalyst MAO was generally less active than DMAC (0.43 vs. 3.37 × 106 g mol^{-1} h^{-1}), but it led to higher molecular weight polyethylenes.

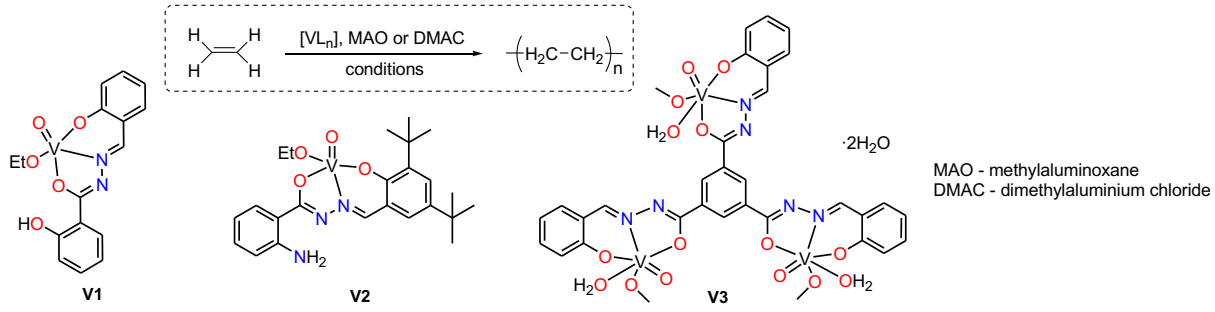

Figure 1. Ethylene polymerization catalyzed by vanadium (V) catalysts **V1-V3**.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P7

IPaintS – Intelligent Coating Sensors for Treating Concrete Structures

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Several concrete structures over the world (e.g. concrete sleepers, dams, bridges, buildings and pavements) have been damaged by chemical expansive reactions, like alkali-silica reaction (ASR), that occurs between reactive silica from aggregates and the alkalis present in the cement paste. The product of this reaction, an alkaline silicate gel, when exposed to liquid water or a humidity greater than 80% expands, causing internal pressures greater than the tensile strength of concrete. This expansion causes the appearance of cracking and in severe cases may lead to rupture. Even with all the existing knowledge on ASR, there's still a lack of solutions for repairing such structures [1, 2].

Focusing on evolving the current state of the art in the field of intelligent coatings for the treatment and detection of this type of concrete pathology, IPaintS project (LISBOA-01-0247-FEDER-047141) was develop directing attention into two main objectives: 1) Study and develop new inhibitors for ASR; 2) Study and develop indicator agents, capable of detecting, at an early stage, its existence. These solutions would incorporate an intelligent coating system composed by one impregnating solution and one coating membrane. In this work an overview of the IPaintS' intelligent coating system will be given, as well as the latest advances obtained.

Figure 1. Concrete railway sleepers affected by ASR.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Centro de Recursos Naturais e Ambiente (CERENA) is a R&D unit funded by FCT through project UIDB/04028/2020. This research was funded by POR Lisboa – Lisbon Regional Operational Program, through Portugal2020, under the scope of the Project "IPaintS - Intelligent Coating Sensors for Treating Concrete Structures" (LISBOA-01-0247-FEDER-047141).

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P8

Cooperation of coordination and halogen bonds in capture of Pd(0)

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The Pd(II) and Pd(0) complexes can serve as Lewis acid and Lewis base catalysts, respectively, to activate covalent bond(s) of a substrate in synthetic transformations.[1] Due to the easy exchange of Pd(II)/Pd(0) redox states in the catalytic cycle, the palladium catalysed cross-coupling reactions to construct C−C or C−heteroatom bonds are among the most powerful and versatile synthetic strategies employed in organic synthesis.

In addition, bifunctional palladium(II) complexes have emerged as highly efficient catalysts for organic transformations. Traditionally, they are prepared by decoration of the secondary coordination sphere, *e.g.,* with noncovalent bond donor or acceptor sites created in the vicinity of the metal centre. But there was no any example of a Pd(0) (as a noncovalent acceptor) and Pd(II) centred bifunctional complex in palladium chemistry, which is prepared for the first time in this work.[1] Due to high directionality, tunability and strength, the halogen bond (HaB) has been employed in engineering the secondary coordination sphere of metal complexes, which can improve their functional properties. Not only common nucleophiles, but a suitable filled d-orbital in a positively charged metal center (Rh^+, Ir^+, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^+, Ag^+ or Au^+) can also act as a HaB bond acceptor. However, the function of a zero-valent palladium centre as a HaB bond acceptor remained unknown. The Pd(II)-mediated reaction of 2,2,2-trichloroacetonitrile with NH_4OH in DMSO affords $Pd^0[Pd^{II}\{NH{=}C(CCl_3)NC(CCl_3){=}NH\}_2]\cdot 2DMSO$ (**1**) (Figure). A cooperation of coordination bond and ∠C–Cl···Pd^0 (2.557 Å and 145.17°) type of halogen bond catches Pd^0 in the crystal structure of **1**. In fact, the Cl···Pd^0 (2.557 Å) distance is longer than the sum of the atomic radii of the interacting atoms (Σr (Cl···Pd^0) = 2.40 Å), and much shorter than the sum of van der Waals radii Σr_{vdW} (Cl···Pd^0) = 3.38 Å.

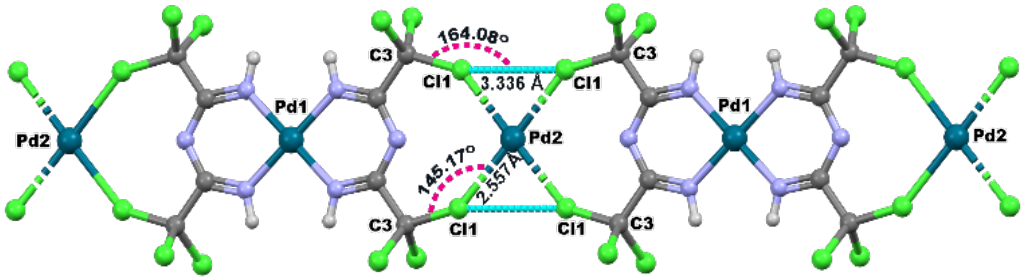

Figure. 1D chains in the solid state of **1**. Due to disorder, DMSO molecules were omitted.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A.V.G. and K.T.M. thank FCT and Instituto Superior Técnico (DL 57/2016, L 57/2017 and CEEC Institutional 2018 Programs, Contracts no: IST-ID/110/2018 and IST-ID/85/2018), as well as to the Baku State University (Azerbaijan).

Reference: [1] A. V. Gurbanov, R. M. Gomila, A. Frontera, N. Q. Shikhaliyev, N. R. Zeynalli, K. T. Mahmudov, A. J. L. Pombeiro, *Angew. Chem., Int. Ed.,* 2023, submitted.

P9

Extraction and characterization of chitin extracted from Black Soldier Fly exuviae and synthesis of biopastics

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Bioplastics are among the sustainable materials that will contribute to the resolution of new and pressing environmental challenges.[1] This work, carried out as part of a master's degree, aims to synthesize chitosan-based bioplastics from Black soldier fly (*Hermetia illucens*) exuviae, in order to achieve an environmentally sustainable product with low production costs. The first challenge was the extraction of chitin from the starting material and its transformation into chitosan ensuring high yield and reduced contamination. Here is presented the characterization by X-ray Photoelectron Spectroscopy of chitin and chitosan obtained from this natural source. Different syntheses of bioplastics, using chitosan extracted by different methods, are also presented.

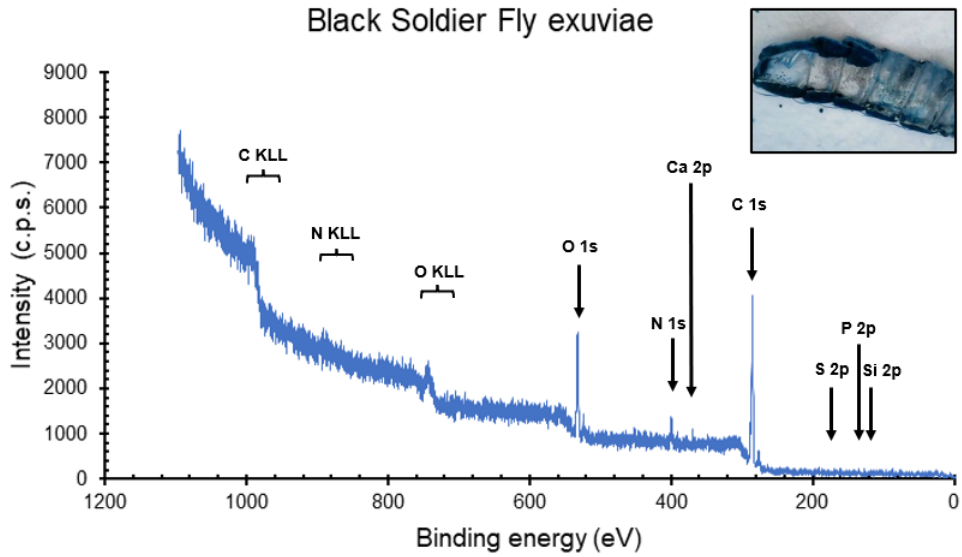

Figure 1. Full XPS spectrum of black soldier fly exuviae. Ca 2p, S 2p, P 2p and Si 2p are hardly perceptible in the wide spectrum. However, the detailed XPS regions attest their presence in residual amounts (below 1 at.%).

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P10

Software tools for a Sustainable Chemistry

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This work aims to analyze the greenness of a chemical process, more specifically the production of adipic acid. 'Green Chemistry' is a term developed in the 90s that supports products and processes that are both economically profitable and beneficial to public health and the environment, thus promoting environmental, social, and economic sustainability. The guidelines to achieve greenness are the 12 Principles of 'Green Chemistry' established in 1998 by Paul Anastas and J.C. Warner [1].

With increasing attention from governmental organizations and society regarding environmental protection, chemistry must have as an intrinsic goal the sustainable development of its industry. The production of adipic acid is an important industry for Nylon 6,6 that can subsequently be applied in the manufacture of fibers and resins.

Based in scientific articles, green metrics results for the reactions involved in the process with the appropriate mass-based and impact-based metrics will be presented.

The goal is to provide meaningful comparisons of different methods used in the production of adipic acid in terms of energy efficiency, minimized use of solvents, process safety, and avoidance of toxic and harmful effects on the environment and human health.

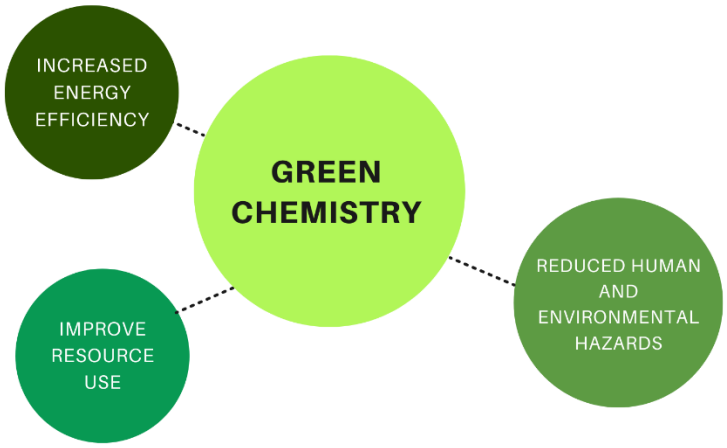

Figure 1. Main goals of Green Chemistry.

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P11

Application of continuous flow chemistry in the synthesis of agrochemical active ingredient metabolites

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The development of plant protection products requires the safety profile analysis of agrochemical active ingredients (AAIs). This includes toxicity determination of AI metabolites. A very common phase-one metabolism reaction is C-oxygenation, catalyzed by cytochrome P450 enzymes[1,2]. The synthesis of oxygenated AAI metabolites is of significant importance to agrochemical producing companies, particularly for ASCENZA Agro[3], as it is necessary for safety evaluation purposes. Furthermore, the transposition of these protocols to continuous flow conditions provides better control of various reaction parameters of the reactions and allows to increase productivity[4].

Herein, we describe the development of a methodology for the synthesis of oxygenated aromatic derivatives of several AAIs in continuous flow conditions, by adapting a method previously described by Tobias Ritter and co-workers[5]. This method allows for the late-stage oxygenation of the aromatic positions by generating mesylate derivatives with bis(methanesulfonyl) peroxide as an oxidant.

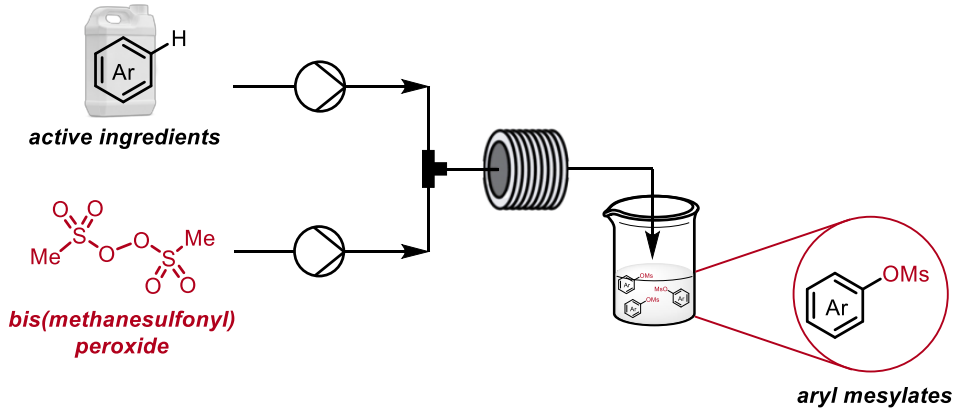

Figure 2. Late-stage aromatic oxygenation of AAIs in continuous flow conditions.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. J.A.S.C. thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND. The authors thank Dr. Ana Viana and Dr. Jorge Correia (CQE-FCUL) for assistance and equipment to perform electrolysis.

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P12

Ni-based activated carbons for CO_2 methanation: On the role of the activation method and ceria incorporation

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CO_2 methanation using green hydrogen constitutes a key catalytic reaction for carbon dioxide emissions abatement and renewable energy storage [1]. Taking into account the high stability of carbon dioxide, the use of catalysts is required. Indeed, catalytic systems based on transition (Ni, Co, Fe) and noble (Ru, Rh) metals supported over Al_2O_3, SiO_2, CeO_2, ZrO_2, hydrotalcites, carbons or zeolites have been reported [2]. While the use of nickel is preferred to noble metals due to the higher availability and lower cost of the first, efforts must be done towards the synthesis of greener supports derived from wastes [2]. Even if the use of activated carbons derived from biomass wastes as support for CO_2 methanation catalysts has been scarcely studied in literature so far, promising results have been reported [3]. Indeed, the performances of these materials were attributed to their high surface area, allowing the storage of high quantities of both H_2 and CO_2.

In this study, three Ni and three Ni-CeO_2-based ACs containing ~20 wt.% of Ni and ~20 wt.% Ce and prepared by incipient wetness impregnation or co-impregnation method were used as catalysts for CO_2 methanation under atmospheric pressure (86100 ml h^{-1} g^{-1}, P_{CO2} = 0.16 bar, H_2:CO_2 = 4:1). Three activated carbons, obtained from coconut shell wastes using chemical ($ZnCl_2$ and H_3PO_4 agents) and physical (CO_2) activation methods, were used as support and characterized by SEM-EDS, N_2 sorption, XRD and TGA. Catalysts were characterized by ICP, N_2 sorption, XRD and TEM. The effects of the activation method for ACs synthesis and the addition of ceria were assessed by carrying out conventional and long-term experiments.

The use of the activated carbon prepared by physical activation led to the best performances both in terms of CO_2 conversion and CH_4 selectivity, which was ascribed to the lower nickel particle size and better basicity of this sample. Furthermore, CeO_2 incorporation was found to significantly reduce Ni^0 particle sizes (reductions in the order of 45-66 %) and likely improve the CO_2 activation capacity of the catalysts. Consequently, an improvement of the activity, especially relevant for the AC support prepared using H_3PO_4 as chemical agent, was observed after addition of CeO_2, with conversions of ~80% at 360 ºC. The most outstanding catalyst, containing Ni and CeO_2 over the AC prepared by physical activation, exhibited similar or better results than other carbons and CO_2 methanation supports from literature. In addition, this catalyst was submitted to a deactivation test at variable conditions for 9 days, being its stability over the time proved. As a result, this work confirmed the suitability of coconut shell biowastes for the synthesis of promising activated carbon supports for CO_2 methanation reaction.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Authors thank Maria Bernardes and Isabel Fonseca from FCT/UNL for providing the activated carbons used as support in this study. Carmen Bacariza thanks FCT for her contract (2020.00030.CEECIND).

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P13

Concrete cracking inhibitory agents using pH-sensitive macrocyclic amines

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Worldwide concrete structures are affected and endangered by expansive chemical reactions, such as Alkali-Silica Reactions (ASR) that causes deleterious expansion of concrete [1]. The result of the reaction between the alkalis present in the cement paste and silica from the aggregates is a gel capable of water absorption. With the continuous ingress of water the gel tends to expand leading to considerable cracking, which endangers the whole concrete structure. Although lithium is known in the literature for its inhibitor effect on this type of reactions, its use in concrete structures still needs tuning [2]. In this work, a novel strategy for successful inhibition of the expansive chemical reactions resulting from ASR is presented. For that, a concrete impregnant solution doped with lithium using macrocyclic amines [3] as pH-sensitive carriers (Figure 1) was developed. Additionally, mechanochemistry was used to prepare the lithium-based inhibitors, so that they could be available also in the solid form, to be used as concrete admixture.

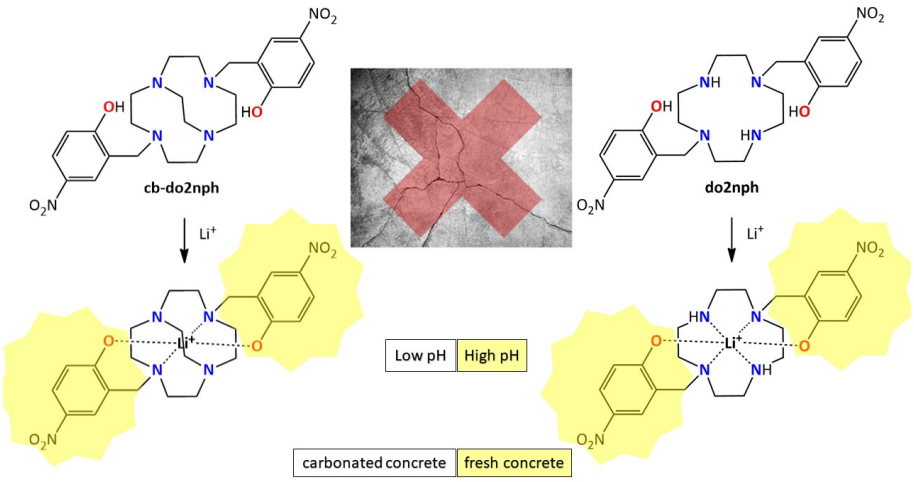

Figure 1. Colorimetric and pH-sensitive concrete lithium carriers.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. CERENA is funded by FCT through project UIDB/04028/2020. This research was funded by POR Lisboa – Lisbon Regional Operational Programme, through Portugal2020, under the scope of the Project "IPaintS - Intelligent Coating Sensors for Treating Concrete Structures" (LISBOA-01-0247-FEDER-047141).

References: [1] A.F. Cristino, M.E.M. Jorge, M.M. Salta, A.S. Silva, *Materials Sci. Forum*, **2008**, *587*, 867–871; (b) J. Custódio, D. Costa, A.B. Ribeiro, A.S. Silva, *Procedia Struct.* **2022**, *37*, 590–597. [2] A.S. Silva, M. Salta, M.E.M. Jorge, M.P. Rodrigues, A.F. Cristino, *Proceedings of the 13 ICAAR*, **2008**, 1250–1259. [3] C.V. Esteves, L.M.P. Lima, P. Mateus, R. Delgado, P. Brandão, V. Félix, *Dalton Trans.*, **2013**, *42*, 6149–6160.

P14

Imineureas production *via* catalytic synthesis using Titanium(IV) ketimide complexes

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Ketimide ligands are well established as support ligands for early transition metals.[1, 2] We have recently synthesized several homoleptic complexes of the type $Ti(N=CR_2)_4$, by reacting $Ti(NMe_2)_4$ with 4 equiv. of $HN=CR_2$ (**1**, Fig. 1). We have demonstrated that in these complexes the ligands display non-innocent behaviour, and suffer insertion of isocyanates, a reactivity pattern that mirrors one previously reported for Thorium chemistry.[3] This insertion reaction is the key to producing imineureas (**2**, Fig. 1) catalytically, that we report here, starting from the commercially available $Ti(NMe_2)_4$. Imineureas are interesting compounds that find applications in industry and pharmacology.[4].

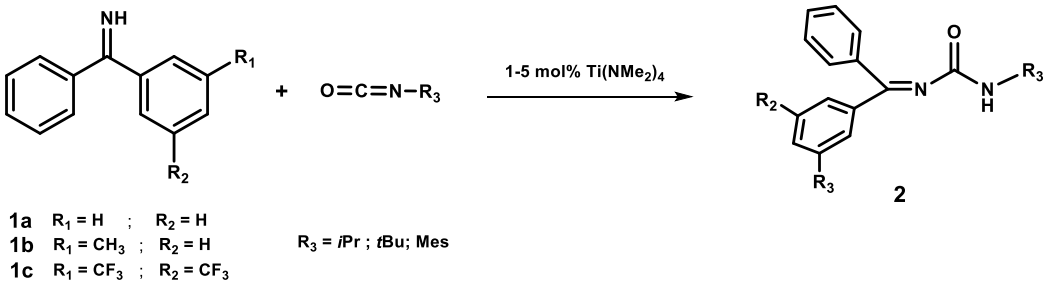

Figure 1. Catalytic reaction of ketimides and isocyanates using $Ti(NMe_2)_4$ as precatalyst

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Fundação para a Ciência e a Tecnologia for a fellowship to C.P.R. (PD/BD/152271/2021).

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P15

Crystallographic Studies to Direct the Self-Assembly Synthesis of Bioactive Coordination Polymers

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Coordination polymers (CPs) have attracted great attention in the field of innovative materials due to their diversity of types, structures, and properties [1]. However, large-scale manufacture of CPs is both a crucial feature for materials science and a limiting constraint. To overcome this issue, a self-assembly synthesis has been widely used for the generation of these materials [2]. In fact, self-assembly methods feature simplicity, flexibility and efficiency, which make them an attractive approach for the large-scale production of CPs, leading to exceptional yields in a single reaction vessel and without the need for extensive purification [3]. However, self-assembly reactions are particularly sensitive to the conditions under which they are performed. Hence, the evaluation of the time necessary for crystallization and/or the monitoring of the type of crystals formed should be considered in the process.

Following our interest in the generation of novel types of functional CPs by self-assembly methods, the present study outlines the synthesis and characterization of two new bioactive silver(I) CPs, $\{[Ag_3(sbda)(NH_3)_2]\cdot\frac{1}{2}H_2O\}_n$ (**CP 1**) and $\{[Ag_3(sbda)(NH_3)_2]\}_n$ (**CP 2**). Both CPs were generated from a silver(I) salt, 5-sulfo-1,3-benzenedicarboxylic acid (H_2sbda) and aqueous ammonia, and characterized by standard methods including single-crystal (SCXRD) and powder X-ray diffraction (PXRD). SCXRD shows that these CPs crystallize in the monoclinic system, space groups $P2_1/c$ and $P2_1/n$. Despite their different crystalline phases, both CPs were formed in the same vessel under identical conditions. PXRD measurements indicate that there is a formation of mixed phases that is guided by crystallization time. The results show that the crystallographic studies play a crucial role in understanding the self-assembly process and can be applied to optimize procedures for guiding the evolution of reaction systems, thus establishing a better control over self-assembly processes.

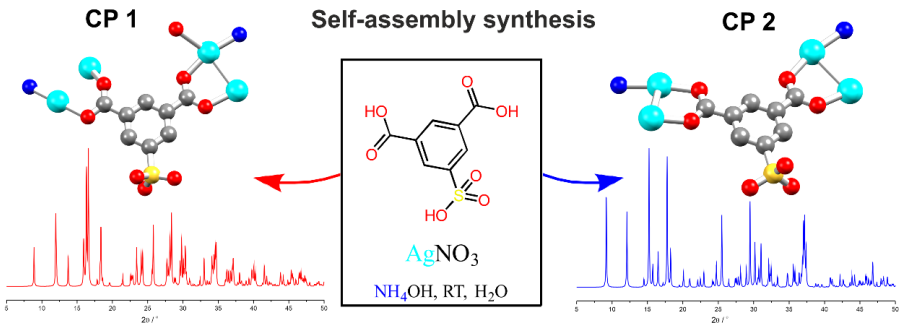

Figure 1. Self-assembly synthesis (middle) and structures of **CP 1** (left) and **CP 2** (right).

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P16

Metal-organic frameworks films for ammonia conversion

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The excessive use of fossil fuels as a response to the energy demand has led to the increase in the concentration of the greenhouse effect gases in the atmosphere contributing to the climate change. Therefore, it is urgently needed to investigate and develop clean and renewable fuel alternatives.

Molecular hydrogen as a non-carbon green fuel is a great alternative due to its accessibility, non-toxicity and higher gravimetric energy density compared to traditional fuels. However, its implementation is hampered due to its properties such as extremely low volumetric energy density, flammability and volatility which leads to challenges in its storage and transportation. One solution to this problem is using a hydrogen carrier such as ammonia, a non-flammable chemical with a well-known storage technology that can be converted to produce N_2 and H_2, while having the advantage of a lower conversion potential when compared with water [1-2]. The focus of this work is the synthesis and immobilisation of metal-organic frameworks (Fig. 1a, MOFs) on electrodes to be used in the electrocatalytic conversion of ammonia to hydrogen, owing its interest to its superb properties of high permanent porosity and potential as catalyst [3].

Two methods of deposition were performed, a direct method (cathodic deposition) which uses the MOF precursors and an indirect method (electrophoretic deposition) where the MOF is previously synthesised. The films (Fig. 1b) formed were characterised by both diffuse reflectance infrared fourier transform spectroscopy (DRIFT) and x-ray diffraction (XRD). Preliminary results of the ammonia conversion using the new films formed as electrocatalysts were obtained using cyclic voltammetry.

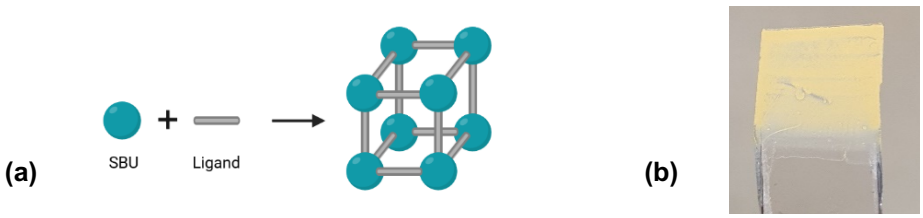

Figure 1. (a) General representation of a MOF structure constituted by the inorganic centre (secondary building unit) and the organic ligand. (b) Example of a MOF film formed using electrophoretic deposition.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021. S.R. acknowledges FTC for financial support (2020.02134.CEECIND).

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P17

Electrochemical cyanation of sparteine

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Synthetic organic electrochemistry presents a valuable opportunity for chemists to conduct highly selective reactions with exceptional functional group tolerance, under mild reaction conditions: Furthermore, it is an environmentally friendly and scalable method [1]. Enhanced reactivity and reproducibility of chemical reactions can be achieved by combining electrochemistry with flow chemistry towards greater control over the reaction parameters [2,3]. Sparteine, a bisquinolizidine alkaloid, has found extensive use as a chiral auxiliary in stoichiometric reactions and as a chiral ligand for lithium, copper, and palladium in asymmetric catalysis [4].

Herein we report a novel method for the electrochemical cyanation of sparteine in batch and in continuous flow. The developed methodology allows for the functionalization of sparteine, yielding several cyano derivatives that are promising intermediates for the development of unprecedented sparteine-based organocatalysts (**Figure 1**).

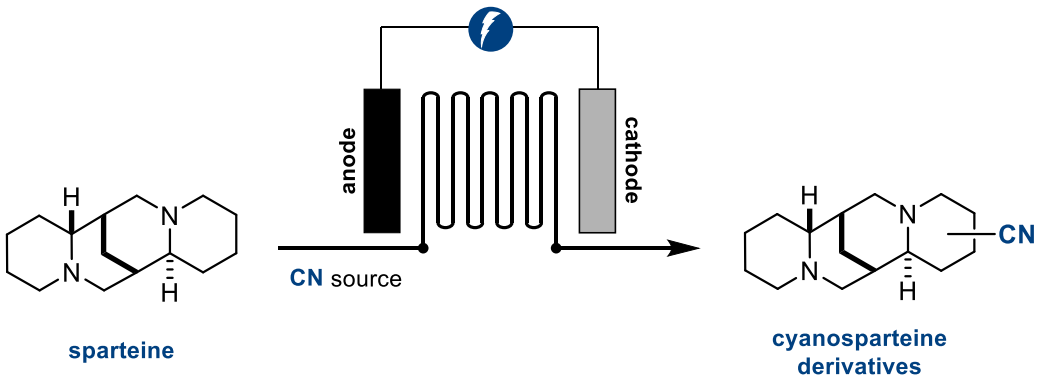

Figure 1. Electrochemical cyanation of sparteine under continuous flow.

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P18

Co(II) and Co(III) coordination compounds for CO_2 photoreduction

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With the continuous increase of global warming and alarming climate changes due to the rise of greenhouse gases emissions, such as CO_2, mainly caused by the colossal industrial pollution, different methods of carbon capture and utilization have been proposed to solve this urgent matter.

Catalysis has been an attractive approach to the conversion of CO_2 into molecules with added value, such as, CO, CH_4, HCOOH and CH_3OH. The homogeneous photoreduction of CO_2 is composed by a catalyst (that in the active form converts the CO_2), a sacrificial electron donor (that donates electrons, and it is stoichiometrically consumed) and a photosensitizer (that absorbs light and mediates the electron transfer between the catalyst and the sacrificial donor). Several compounds using different metallic centers (usually transition metals) and different ligands have been studied in the photoreduction of CO_2. Among the transition metals, Mn, Re, Fe, Co and Ni are the most commonly used in as catalysts for the photoreduction of CO_2.

We present the synthesis and characterization of different Co(II) and Co(III) complexes based on different imine and amine ligands. These compounds were analyzed by Fourier Transform Infrared spectroscopy (FTIR) and Ultraviolet-Visible spectroscopy (UV-vis), cyclic voltammetry (CV) and nuclear magnetic resonance (NMR). We also investigated their ability for CO_2 photoreduction.

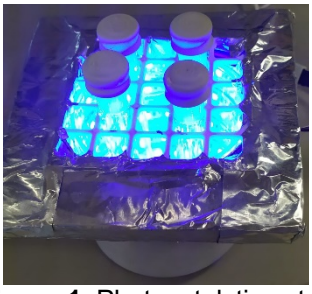

Figure 1. Photocatalytic setup

Figure 2. Crystals of catalyst

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P19

Isomerization of limonene to high added value products over optimized sulfonated carbons

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The use of renewable raw materials from agricultural resources for the production of organic compounds has been extensively investigated. Among the alternatives, the use of terpenes as a renewable resource has shown potential for the production of these compounds with high added value. Brazil is one of the major world producers of orange essential oil, in which the main constituent is the terpene called limonene [1]. The isomerization of limonene produces terpene compounds with high added value, such as: terpinolene, α-terpinene and γ-terpinene, as well as p-cymene. These products have great applicability in the food, cosmetics, polymers and chemical industries[2]. In this context, this work used sulphonated carbons in the study of limonene isomerization. The preparation of sulfonated carbons was optimized using the Rotational Central Composite Design (DCCR). Eleven different experiments were investigated and correlations between synthesis conditions and catalytic performance were identified. The in-situ carbonization and sulfonation process was found to be promising in preparing sulfonated carbons, as sulfonated carbons with Brønsted acid characteristics active in Limonene isomerization were obtained. It was possible to reach, after 2h of reaction at 150ºC, 94% of limonene conversion, with 35, 16 and 13% of yield of α-terpinene, γ-terpinene and terpinolene, respectively, p-cymene, was also produced, but in smaller quantities. Reactions were carried out without solvent. Planning via DCCR allowed evaluating the effect of variables on catalyst preparation. When analyzing the catalytic results via DCCR, the possibility of a synergistic relationship between accessible sites and textural properties was observed, which may facilitate the transmission of limonene emissions to active sites. This optimization evaluated optimal conditions for the amount of H_2SO_4 and the temperature used in the synthesis of the material, showing that it is possible to reduce the temperature and the amount of H_2SO_4, allowing energy reduction and reduction of used reagents, transformed in the preparation of a low-energy catalyst. cost under mild conditions.

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P20

CO_2 methanation in cement sector: Assessing catalysts performance under oxygen and steam-containing feeds

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The hydrogenation of carbon dioxide for the production of synthetic natural gas, CO_2 methanation, can be considered as a key reaction for the storage of surplus renewable electricity in the form of energy vectors such as methane. This process is particularly interesting for cement industries, responsible of ~8% of global carbon dioxide emissions, as they could re-use this synthetic natural gas in the process and promote circularity while reducing carbon emissions in this sector [1]. CO_2 methanation is typically carried out using metal-supported catalysts, being Ni the most commonly studied active metal. Concerning the supports, the use of zeolites, mainly with Ni as active metal, has revealed promising results. Guaranteeing catalysts activity, selectivity and stability under realistic CO_2 methanation conditions is essential for the implementation of this process in cement industry. Indeed, the presence of oxygen, steam or even sulfur compounds in the CO_2 methanation feed could be responsible for severe catalysts deactivation, especially when working with Ni-based systems [2]. Thus, performing systematic studies to test the influence of minor compounds typically present in real effluents (e.g., oxygen, steam) in the performances of CO_2 methanation catalysts containing different active metals is key.

In this study, two Ru/Zeolite and Ni/Zeolite catalysts were synthesized using an optimized support by incipient wetness impregnation method. The preparation conditions used in terms of metal loading and thermal treatment were optimized in previous studies. Metal-containing catalysts were characterized by XRD, H_2-TPR, N2 sorption and TGA, being finally tested towards CO_2 methanation using different feed compositions ($CO_2/H_2/N_2$, $CO_2/H_2/O_2/N_2$ and $CO_2/H_2/H_2O_{(v)}/N_2$) keeping the total flow, the catalyst mass and the CO_2 and H_2 partial pressures as constant. For comparison purposes, a commercial CO_x methanation catalyst (Ni/Al_2O_3) was also characterized and tested under the conditions previously described.

Results indicated that Ru was incorporated as RuO_2 over the zeolite (H_2-TPR), while NiO was identified in Ni/Zeolite sample (XRD and H_2-TPR). After reduction, the presence of Ru^0 and Ni^0 sites was guaranteed in the materials, with average particle sizes in the order of 20 nm verified by TEM. Furthermore, both catalysts presented high hydrophobic surfaces (h indexes >0.90; TGA). Catalytic results indicated that oxygen presented a negative impact on the performances of all samples, which was attributed to the competition of H_2/O_2 reaction with the CO_2 methanation and to the re-oxidation and/or sintering of the catalyst's active sites. In the case of steam, no remarkable impacts on the results were verified, probably due to catalysts' hydrophobic properties.

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P21

Heterometallic Cyanometallate-driven Coordination Polymers: Self-assembly, Structural Features, and Magnetic Properties

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In recent decades, much interest has been focused on the design of metal-organic frameworks and coordination polymers using a large variety of metal nodes and organic linkers. In particular, an interesting research direction concerns the heterometallic coordination compounds containing cyanometallate linkers on account of their promising magnetic behavior. Potential applications for such materials include data storage, quantum computing or molecular spintronics. Hexa- and tetra-cyanometallates, $[M(CN)_6]^{3-}$ and $[M(CN)_4]^{2-}$, have been extensively applied as attractive building blocks to interact with coordinatively unsaturated transition metal ions and construct a variety of coordination polymers (CPs) with remarkable magnetic behavior, including single-molecule (SMM), single-chain (SCM) magnetism or photomagnetism.[1−3]

In this study we report our recent results on the synthesis and characterization of new heterometallic coordination compounds. The crystal structures of several products have been determined including the alkoxo-bridged dicopper Cu(II)/Ni(II) CPs $[Cu_2(dmea)_2Ni(CN)_4]_n{\cdot}nH_2O$ and $[Cu_2(bdea)_2Ni(CN)_4]_n$ with dimethylethanolamine and butyldiethanolamine ligands, Cu(II)/Co(III) CPs $[\{Cu_2K(H_2tipa)_2\}Co(CN)_6]_n{\cdot}8nH_2O$ and $[\{Cu_2(H_2tea)_2\}_3\{Co(CN)_6\}_2]_n{\cdot}10nH_2O$ with triisopropanolamine and triethanolamine ligands, as well as a discrete Cu(II)/Fe(III) coordination compound $[Cu_4(bistris)_4][Fe(CN)_6]{\cdot}5H_2O$ bearing bis-tris methane as a ligand. Structural features and magnetic properties of these compounds were investigated. In particular, magnetic susceptibility data for one of the Cu(II)/Ni(II) CPs reveal a strong antiferromagnetic interaction between the Cu(II) ions in the dimer units (exchange coupling parameter *J* values are between -200 and -400 cm^{-1}).

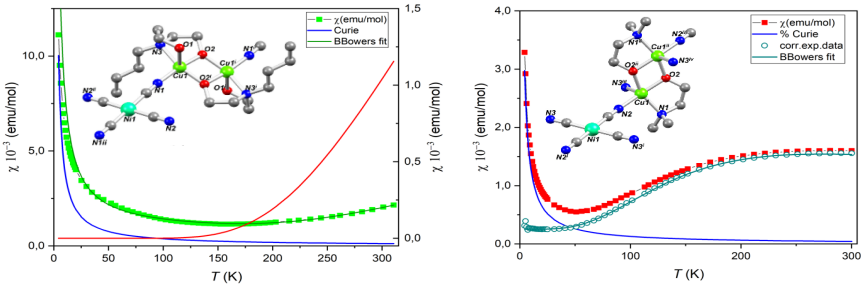

Figure 1. Temperature dependence of χ for $[Cu_2(bdea)_2Ni(CN)_4]_n$ (left) and $[Cu_2(dmea)_2Ni(CN)_4]_n{\cdot}nH_2O$ (right) and fitting with the Bleaney-Bowers model.

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P22

Reaction of *bis*(2,4-*bis*(trichloromethyl)-1,3,5-triazapenta-dienato)-Zn(II) with pyrazole, 4,4'-bipyridine and Cu(acac)$_2$

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Four coordinate transition metal complexes adopt tetrahedral, trigonal pyramidal, see-saw or square planar geometries.[1] Reactivity and functional properties of metal complexes are dependent on many factors, including the coordination geometry of the metal centre.[2] Not only ligands, but the metal centre itself can also dictate the coordination geometry in metal complexes. For example, the coordination geometry of Cu(II) and Zn(II) in [M{NH=C(CCl$_3$)NC(CCl$_3$)=NH}$_2$] (M = Cu (**1**),[3] Zn (**2**)[4]) is a square planar and a trigonal pyramidal, respectively. These differences for the preferred coordination environment at the primary coordination sphere of metal complexes naturally impact their crystal and supramolecular structures, functional properties, and reactivity. Herein, we have studied the reaction of **2** with pyrazole (in methanol), 4,4'-bipyridine (in DMF) and Cu(acetylacetonate)$_2$ (in DMF), which lead to the new Zn(II) complexes [Zn$_2$(μ_2-pyrazolato)$_2$\{NH=C(CCl$_3$)NC(CCl$_3$)=NH}$_2$] (**3**), [(Zn(μ_2-4,4'-bipyridine)\{NH=C(CCl$_3$)NC(CCl$_3$)=NH}$_2$)·2(DMF)]$_n$ (**4**) and [Cu\{NH=C(CCl$_3$)NC(CCl$_3$)=NH}$_2$]·2DMF (**5**), respectively (Figure). These new compounds (**3**–**5**) were fully characterized by IR, ESI-MS, elemental analysis, and X-ray diffraction, and will be applied as catalysts in cycloaddition of CO_2 with epoxides.

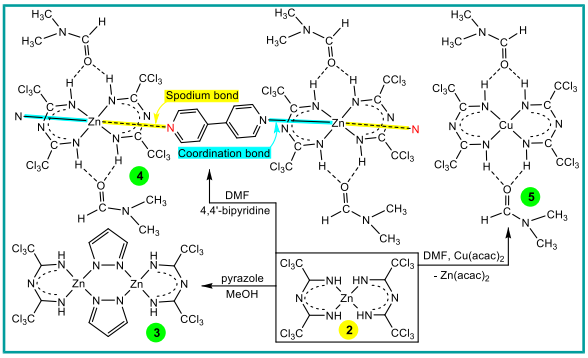

Figure. Reaction of **2** with pyrazole, 4,4'-bipyridine and Cu(acac)$_2$.

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P23

Highly Efficient Mechanochemical Synthesis of Metal-Free and Hybrid Perovskites

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Perovskites are incredibly versatile compounds that derive from the parent formula ABX_3, as shown in Figure 1. They are extensively applied to photosensitive devices such as solar cells, LEDs, photocatalysis and sensors [1]. A significant drawback when it comes to these compounds is their synthesis. Usually, they involve high temperatures, toxic solvents, and large amounts of time to form crystals, in most cases, with low yields and purity [2]. To overcome all these issues, mechanochemistry has been used as an emerging tool for their synthesis, decreasing the time of reaction from days into minutes and low purities into meaningfully high purities, resulting in a fast, eco-friendly, and efficient method [2].

In this work it has been attempted to synthesize metal-free and hybrid perovskites using 1,4-diazabicyclo[2.2.2]octane (DABCO) as A and Cl to X, while NH_4Cl, $CoCl_2 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ where used as the framework of octahedrons for metal-free and hybrid perovskites respectively.

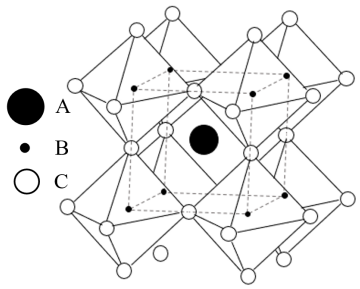

Figure 1. Perovskite Stucture

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A doctoral grant awarded by the FCT to I. Feliciano (2021.04637.BD) is also gratefully acknowledged.

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P24

Nanocomposites used as catalysts in ultrasound-assisted peroxidative oxidation of primary and secondary alcohols

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Composites are a combination of two or more materials, usually with different physical or chemical properties, normally with improved properties compared to the individual components. Nanocomposites are those composites in which at least one of the constituents has nanoscale morphology (<100 nm). A Core-shell is a structured nanocomposite consisting of a nanoparticle coated with a different material [1]. Core-shell containing a spherical core of magnetite (Fe_3O_4), an iron oxide nanoparticle, exhibits superparamagnetic properties which allow easy recovery of this material since only a magnet is needed for its extraction [2]. Being aware of this advantage, different spherical ferrimagnetic core–shell nanocomposites surrounded by different shells were synthesized and explored as catalysts for the peroxidative oxidation of different primary and secondary alcohols.

In pursuit of our interest in the catalytic oxidation of alcohols, we show the catalytic performance of Fe_3O_4-based nanocomposites, namely Fe_3O_4@TiO_2, Fe_3O_4@CaO, Fe_3O_4@CuMOF in the ultrasound-assisted peroxidative oxidation of 1-phenylethanol and of benzyl alcohol. All compounds were characterized by IR, SEM and EDS elemental mapping. The effect of various parameters such as type of solvent, type of oxidant (TBHP and H_2O_2), time, and amount of catalyst were studied towards the optimization of the catalytic process.

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P25

Modeling preferential solvation in aqueous binary mixtures using 2-chloro-2-methylpropane as a kinetic probe

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Solvent effects in organic reactions remain one of the most fascinating topics in chemistry. Our research group (as well as others) has been interested in the application of quantitative structure-property relationships to the study of tertiary alkyl halides' reactivity in different media [1-5]. In particular, the reaction of 2-chloro-2-methylpropane (2-Cl-2-MePr) in several aqueous binary mixtures has been used along with that of other tertiary alkyl halides to probe solvation and mechanistic features [6] and to test hydrophobic effects and preferential solvation aspects [7,8].

Several models have been developed over the years to explain and quantify preferential solvation in solvent mixtures. One of those is the well-known and quite successful Bosch and Rosés model, originally applied to binary mixtures [9] and later extended to ternary and higher order mixtures [10].

In this work, Bosch and Rosés's model was applied to the obtained or collected -log *k* (2-Cl-2-MePr) *vs.* x_w (mole fraction of water) values in several protic-water and aprotic-water binary mixtures at 25 °C. The obtained curves exhibit preferential solvation and synergistic patterns (*e.g.,* Figure 1) which will be presented and discussed.

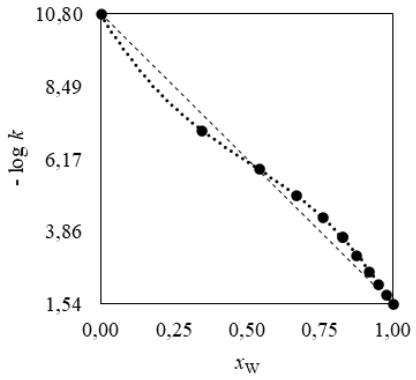

Figure 1. -log *k* (2-Cl-2-MePr) *vs.* x_w in 1,4-dioxane-water mixtures at 25 °C.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P26

CO_2 reduction using Fe(II) complexes

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CO_2 is one of the main greenhouse gases in the Earth's atmosphere. Currently, there is a huge interest in developing strategies to capture and convert it into chemicals with economical value.[1] CO_2 reduction can be performed recurring to different technologies, such as electroreduction, photochemical reduction among others. Photochemical catalysis and plasma technology have been looked at as promising methods for CO_2 conversion operating at ambient pressure and temperature, and converting CO_2 into products such as CO, CH_4 and CH_3OH. [2-4] In CO_2 conversion, different types of molecular complexes or materials can be used as catalysts based in different metal centers. [5] Our work aims to synthesise new Fe(II) complexes for CO_2 photoreduction and plasma CO_2 conversion comprising homogeneous (molecular Fe(II) catalyst) and heterogeneous (MOFs functionalised with Fe(II) complexes) approaches. Here we present our preliminary results on the photoreduction of CO_2 to CO using visible light and the limitations in selecting a suitable photosensitiser to promote efficient electron transfer to the Fe(II) catalysts.

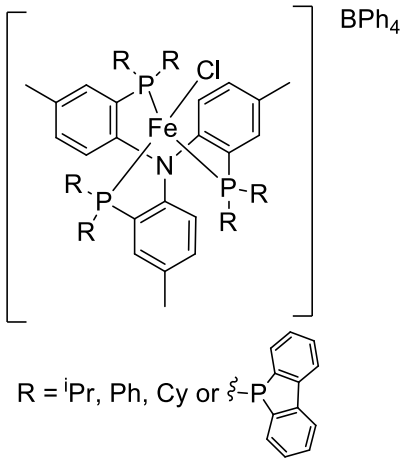

Figure 1. Fe(II) complexes used as catalyst in this work.

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P27

Revisiting solvent effects on the solution enthalpies of 3-methylimidazolium tetrafluoroborates: a QSPR comparative study

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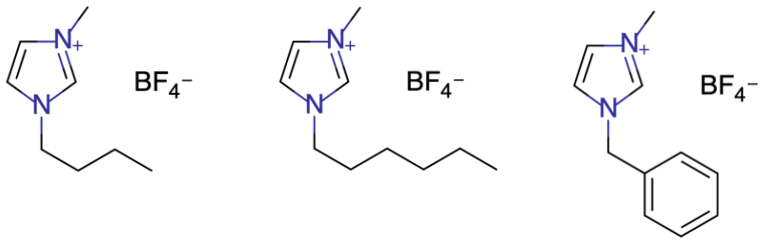
A quantitative structure-property relationship (QSPR) methodology was used in a previous work [1] to analyse solvent effects on solution enthalpies at infinite dilution ($\Delta_{sol}H^{\infty}$) of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate (Figure 1, a). Results of that work suggested that a more robust QSPR model was required to gain a deeper insight into the referred thermochemical process.

Aiming at obtaining a better understanding of these type of processes, the ILs (a) 1-butyl-, (b) 1-hexyl-, and (c) 1-benzyl-3-methylimidazolium tetrafluoroborates (Figure 1) were similarly studied in the present work using two QSPR equations, namely the KAT [2] and the *m*KAT equations [3]. According to these equations, interactions between solute and solvent are quantified by the following terms: an hydrogen bond donor (HBD) acidity parameter (α), an hydrogen bond acceptor (HBA) basicity parameter (β) and a polarizability/dipolarity parameter (π^*). In the *m*KAT, the latter is subdivided into two components: a polarizability (*DI*) and a dipolarity (*Dip*) contribution.

An extra parameter, *C*, was added to both equations to account for solvent-solvent interactions due to the disruption and/or reorganization of solvent structure associated with the formation of a cavity to accommodate the solute, thus yielding the models dubbed as KAT+*C*, also known as TAKA [4], and *m*KAT+*C*, respectively.

Applying these model equations and comparing their results allowed the elucidation of solvent effects on the solution enthalpies of the three compounds, as well as a better understanding of the real contribution of each parameter to the overall process.



(a) (b) (c)

Figure 1. (a) 1-butyl-, (b) 1-hexyl-, and (c) 1-benzyl-3-methylimidazolium tetrafluoroborates.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P28

Synthesis of *C*-glycoside Analogues with Potential against Carbapenem-resistant Gram-negative Bacteria

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The search for effective compounds against carbapenem-resistant (CR) Gram-negative bacteria is a top priority due to the high case fatality rates and the lack of therapeutic choices for infections caused by these pathogens [1]. In a recent proof-of-concept study, 1-(4,6-dideoxy-α-D-*xylo*-hexopyranosyl)dodecane (**1, Figure 1**) has shown promising antimicrobial activity against a broader variety of CR Gram-negative clinical isolates than the corresponding *O*-glycoside (**2, Figure 1**), requiring lower colistin concentrations for outer membrane permeabilization and exhibiting a potential for lower cytotoxicity [2]. Hence, the present work focuses on the synthesis of a small library analogues of **1** for structural optimization and structure-activity relationships against CR Enterobacteriaceae (CRE), *P. aeruginosa* (CRPA) and *A. baumannii* (CRAB), in combination with colistin. As changes in the lipophilic tail have not been extensively explored so far, we herein focused on the scale-up synthesis of the 4,6-dideoxy sugar precursor bearing an allyl moiety in the anomeric position (**3, Figure 1**) for further derivatization via metathesis, using the 2nd generation Grubbs-Hoveyda catalyst. As for glycone modifications, we will present the synthesis of a 4,6-cyclo-4,6-dideoxy-α-D-*galacto* analogue precursor (**4, Figure 1**) for subsequent C-glycosylation, which will allow a direct comparison between the 4,6-cyclo and the classic 4,6-dideoxy pattern of the lead scaffold. All synthesized compounds will be tested in top-priority CR Gram-negative bacteria as well as in eukaryotic cell lines to assess the effects of the proposed structural modifications, hopefully leading to the identification of innovativ molecular entities with improved activity, reduced cytotoxicity, and potential for pharmaceutical development in combination with colistin.

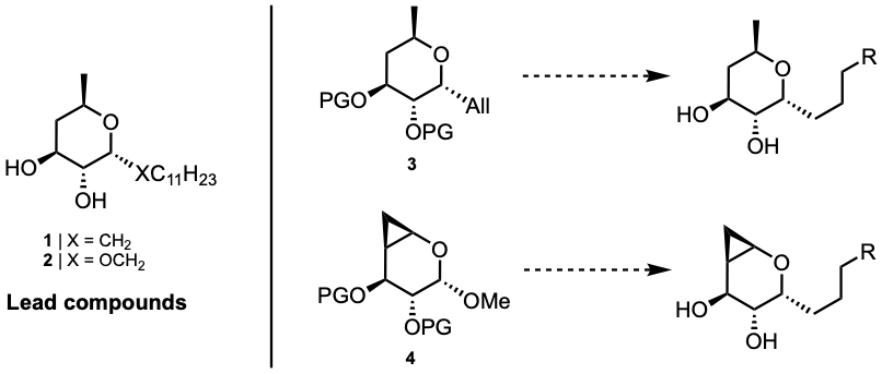

Figure 1. Lead compounds and target structures of the present work.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Ana Marta de Matos wishes to thank FCT for funding through the Individual Call for Scientific Employment Stimulus (2022.07037.CEECIND).

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P29

Synthesis and characterization of magnetic MOFs

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Metal-organic structures (MOF) are crystalline polymers with nanopores, created by the combination of organic molecules that react with inorganic metal ions, forming a three-dimensional structure, with covalent bonds [1].

Due to the interconnected voids at the nanoscale, these structures have an unparalleled potential to trap, store and catalyze ions and molecules that can be harmful to the environment, such as carbon dioxide [1].

In this work, the synthesis and characterization of several MOFs with magnetic properties will be discussed. The comparison between MOFs produced by solvent-free grinding and mixing with magnetic particles versus in-situ synthesized magnetic MOFs will be presented.

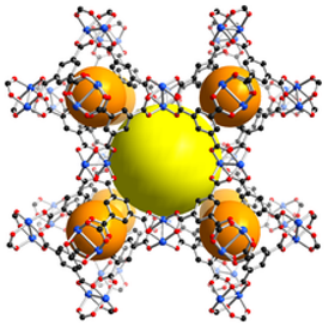

Figure 1. Framework structure of desolvated HKUST-1. The spheres represent two different types of pores within the framework structure. Blue: metal, red: oxygen, black: carbon.

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P30

Sol–gel-Derived Synthetic CaO-Based Materials for Thermochemical Energy Storage

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The use of renewable energy (RE) sources is crucial to reduce the negative impact of greenhouse gas emissions, but the RE intermittency is a huge disadvantage that can be overcome through the development of thermochemical energy storage (TCES) technologies. The calcium looping (CaL) based on the cyclic carbonation and calcination of $CaO/CaCO_3$ pair, using CO_2 as working fluid is a promising technology due the $CaCO_3$ availability, low price, and high energy density (1790 kJ/kg $CaCO_3$). When the production of energy is required, the CaO and CO_2 stored reactants are brought together at the necessary conditions to drive the exothermic carbonation reaction [1]. The development of highly reactive and stable materials is urgent for a faster upscale and implementation of CaL based process for TCES.

The objective of this work was obtaining materials with higher porosity and stability for CaL than the observed with the natural materials, through the synthesis of doped and undoped CaO-based materials by the sol-gel method. The CaL experiments were carried out in a fixed-bed unit over 10 calcination-carbonation cycles, with calcination and carbonation temperatures of 930 °C and 800 °C, respectively. The selected dopant materials were: Methocel^{TM}, SiC, MgO and CeO_2. The effect of doping fraction was assessed through the synthesis of 10/90, 20/80 and 30/70 mixtures of dopant/CaO. TGA, XRD, SEM, and N_2 adsorption techniques were used to examine mineralogical, textural, and morphological properties before and after the 10 cycles.

The best results were obtained by the MgO/CaO-doped material, more specifically with 10 % of MgO where a heat storage density (HSD) of 1088 kJ/kg of $CaCO_3$ was attained after 10 cycles (corresponding to a CaO conversion of 61%), while for the undoped material the HSD was 878 kJ/kg of $CaCO_3$. Comparatively with the performance of natural geological and waste-based materials tested in a previous work [2] the HSD increases between 143 and 470 %, for waste marble Galrão and marble Estremoz, respectively. The results are encouraging and the use of sol-gel method to synthetize more reactive and stable materials for TCES is an alternative for TCES. Future studies will be complemented with techno-economic analysis (TEA).

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Authors thank also the FCT for funding the Solar-driven Ca-Looping Process for Thermochemical Energy Storage (PTDC/EAM-PEC/32342/2017) project.

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P31

Oxidative desulfurization of sulfur compounds with Molybdenum supported catalysts

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The production of green fuels has been gaining more importance due to increased awareness of the adverse effects of burning sulfur containing fuels on human health and environment. The removal of sulfur compounds is imperative to produce green fuel oils and to meet the new requirements of sulfur standard contents (10–15 ppm).[1-2] Oxidative desulfurization (ODS) is considered a promising and highly efficient method owing to its mild operation conditions and high efficiency. Generally, ODS includes mainly two steps: (1) an appropriate agent oxidizes the organic sulfur compounds to sulfoxides and/or sulfones; (2) the oxidation products were removed by suitable methods. Using this approach several researchers are developing cost-effective and environmentally friendly methods for ODS desulfurization, which is still a challenge. In this work, a new material was developed and characterized to be used as a catalyst in the oxidative desulfurization of sulfides. The catalyst was prepared by supporting the precursor complex $MoI_2(CO)_3(MeCN)_2$ on iron oxide nanoparticles shelled with silica and modified with an organic moiety. The NPM_{30}-Si-inic-Mo nanomaterial was obtained and characterized by infrared spectroscopy (FTIR) and X-ray powder diffraction (DRX) and by Scanning Electron Microscopy (SEM) and Transmission (TEM). The NPM_{30}-Si-inic-Mo was tested as catalyst in the oxidation of four sulfides (diphenyl and methyl phenyl sulfide, dibenzothiophene and 1-benzothiophene). All reactions were carried out at 80 °C, varying the oxidant (*tert*-butyl hydroperoxide or H_2O_2) as well as the substrate:oxidant ratio (1:1 or 1:2 mmol). In general, it was found that the oxidation to sulfoxide and sulfone occurred, and the most promising oxidant to obtain the sulfone was TBHP. The reaction of phenyl methyl and diphenyl sulfide allows to obtain 98 and 34% yield when were used 2 mmol of oxidant, respectively. The catalytic tests revealed promising results, and the possibility of recovering the catalyst in some reactions, through a magnet, was tested, in which it was verified that, after its removal, the resulting solution was clear.

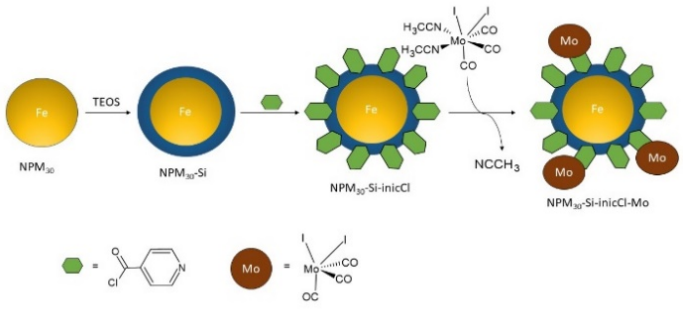

Figure 1. Catalyst synthesis steps

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P32

Water-soluble mixed-valence cobalt(II,III) complex as a homogeneous catalyst for the mild peroxidative oxidation of toluene

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A mixed-valence cobalt(II,III) complex, [{Co(1κ*N*,*O*^{2}-L)(1κ*N*,*O*^{2}:2κ*O*-μ-L)}$Co_{0.5}(H_2O)_2]_2$•$10H_2O$ is formed when $Co(NO_3)_2 6H_2O$ reacts with 2-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)benzoic acid in methanol. The trinuclear compound was fully characterized by IR spectroscopy, ESI-MS, elemental, and single-crystal X-ray diffraction analysis [1]. Following our interest in the catalytic oxidation of VOCs (Volatile Organic Compounds) [2-4], the catalytic performance of the water-soluble mixed-valence cobalt(II,III) complex was investigated for the peroxidative oxidation of toluene (model VOC) with *tert*-butyl hydroperoxide, under mild conditions (Figure 1). Besides conventional heating, other energy inputs, *i.e.*, ultrasound- and microwave-assisted methods were explored. The effects of a series of parameters were studied to improve the catalytic reaction and under optimized reaction conditions a total product yield of *ca*. 38% (benzyl alcohol + benzaldehyde + benzoic acid) was achieved.

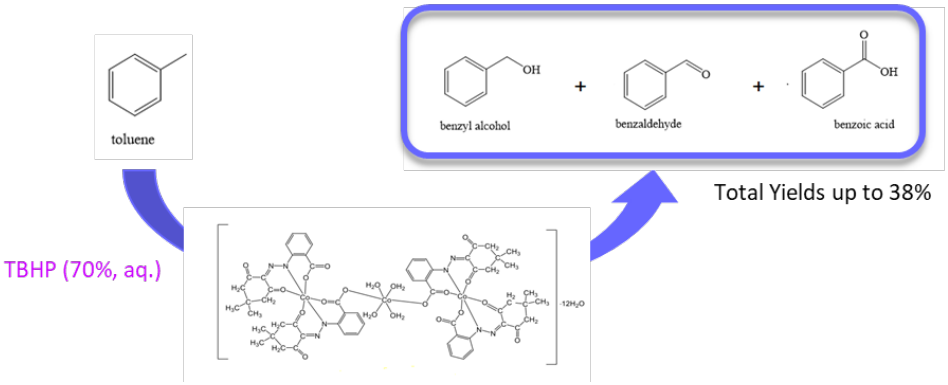

Figure 1. Peroxidative oxidation of toluene

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This work also was supported by the National Natural Science Foundation of China [52125605] and the Fundamental Research Funds for the Central Universities [2022ZFJH004], China; and by the Fundação para a Ciência e Tecnologia, Portugal through the [2022.02069.PTDC project and by the Instituto Politécnico de Lisboa [IPL/2022/MMOF4CO2_ISEL project].

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P33

CO_2 valorisation with earth abundant metals and cryptates

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CO_2 plays a crucial role in the carbon cycle, which keeps the Earth's temperature stable. The expansion of the human population and the energy demand, increased Earth's CO_2 concentration unbalancing the carbon cycle, affecting our planet's energy balance. This led to the urgency of finding efficient pathways of carbon utilisation and recycling to form valuable products.

Molecular activation is crucial in chemical and biological systems, where CO2 is one important player. Thus, researchers and industries had a deep interest in creating catalysts that, by electro- and photoreduction, can convert CO_2 either into liquid fuel precursors (carbon monoxide and hydrogen) [1] or directly to liquid fuels (methanol and/or methane). [2]

The photoconversion of CO_2 can be made in homogeneous and heterogeneous media. The former has the advantage of modulating the catalytic active sites to improve selectivity. It requires three components: the catalyst (CAT, which in the active form, converts CO_2), the sacrificial donor (SD, donates electrons and is consumed) and the photosensitiser (PS, absorbs light and mediates the electronic transfer between the CAT and the SD).

Our research group reported Co(II)-cryptates, catalysts, with different substituents in the aromatic rings (-Br, -NO_2, -CCH) and observed that the capture and conversion of CO2 were affected by them. [3]

We present the synthesis and characterisation of Co(II)/Co(II), Co(II)/Zn(II) and Fe(II)/Zn(II) cryptates previously synthesized and new ones with different substituents in the aromatic rings (-H, -Br, -NO_2, -CCH, -I and -OCH_3). The photoreduction of CO_2 and the photocatalytic system and setup was also investigated.

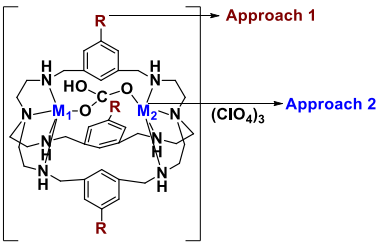

Figure 1. Dinuclear Co(II)/Co(II), Co(II)/Zn(II) or Fe(II)/Zn(II) cryptate with ClO_4^- as anion.

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P34

Effect of substituents on the chalcogen bonding in 5-substituted benzo[*c*][1,2,5]selenadiazoles and their copper(II) complexes

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The chalcogen bond (ChB) is a noncovalent attraction between an electrophilic chalcogen atom and a nucleophilic (Nu) region in the same (intramolecular) or another (intermolecular) molecular entity: R−Ch···Nu (Ch = O, S, Se or Te; R = substituents; Nu = nucleophile). Both strength and directionality of ChB are comparable to the hydrogen and halogen bonds, and depend on substituents, nature of the Ch atom (tunability), hypervalency and nucleophilicity of the interacting partner.[1,2] ChB is a new player in the decoration of the secondary coordination sphere of metal complexes, which concerns an important synthetic strategy in the crystal engineering, catalyst design, etc. Herein, we have studied the effect of electron withdrawing and donating substituents on the strengths and directionality of ChB in 5-substituted benzo[*c*][1,2,5]selenadiazoles (**L$^{1-3}$**) and their copper(II) complexes (**1**−**3**). The Se···N (2.837−3.155 Å) distance is much shorter than the sum of van der Waals radii of the interacting atoms Σr_{vdW} (Se···N) = 3.45 Å, although there is no trend between this ChB distance and the Hammett's substituent constant (σ_p) in **L$^{1-3}$** as well as in **1**−**3** (Figure). The ∠N−Se···N angle increases in the following order 165.60° (−Cl) < 169.16° (−H) < 170.30° (−CH_3) in **L$^{1-3}$**, but this trend was interrupted in **1**−**3** (Figure).

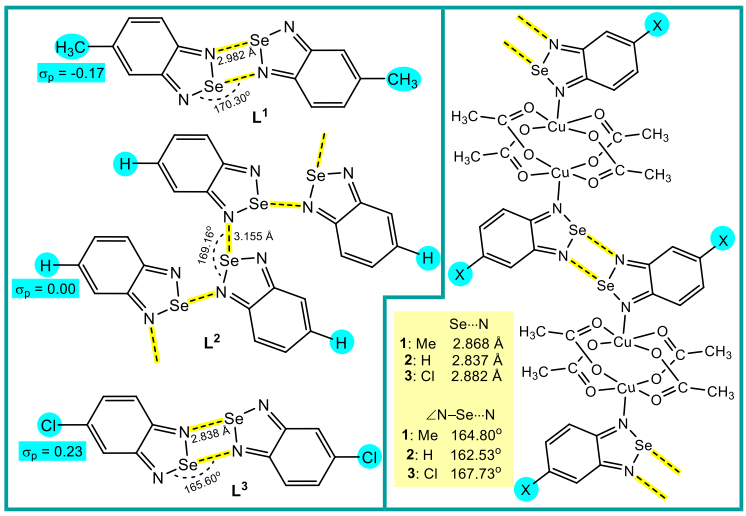

Figure. Chalcogen bonding in 5-substituted benzo[*c*][1,2,5]selenadiazoles and their copper(II) complexes.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. VAA is grateful to Associação do Instituto Superior Técnico para Investigação e Desenvolvimento for her research fellowship through grant no: BL110/2022-IST-ID. A.V.G. and K.T.M. thank FCT and Instituto Superior Técnico (DL 57/2016, L 57/2017 and CEEC Institutional 2018 Programs, Contracts no: IST-ID/110/2018 and IST-ID/85/2018), as well as to the Baku State University (Azerbaijan).

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P35

Glycerol Mixtures

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Biofuel is the ecological solution to the future lack of traditional fuels. The work consists of studying the reactions of glycerol with ionic liquids to determine its density with respect to temperature. The objective is to find if it is viable to be used as fuel. To determine density, we have changed some parameters like temperature and mixture with different ionic liquids. The solubility of solutions was being tested already.

In this poster I will present the results (Figure 1) for the pure componentes and for mixtures at different temperatures.

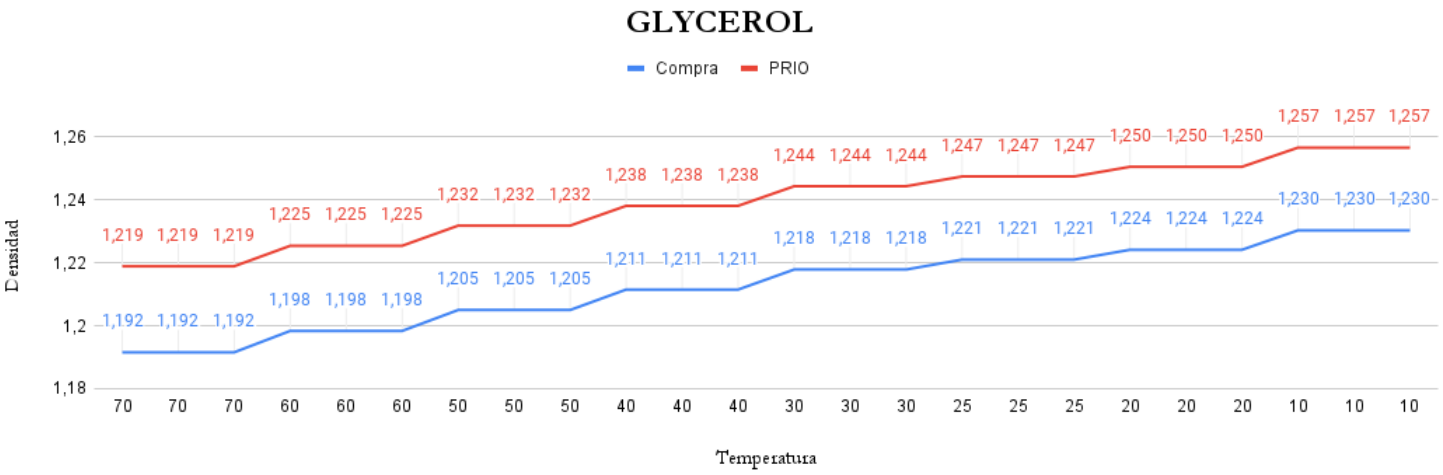

Figure 1. Comparison of the density of glycerols.

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P36

Polyaromatic Group Containing Cd(II)-based Coordination Polymers for Adsorption and Catalytic applications

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Coordination polymers are crystalline coordination networks consisting of metal ions or clusters and multidentate organic ligands [1]. This area of research is currently undergoing a rapid growth due to their potential applications as functional materials in gas storage, molecular separation, heterogeneous catalysts, magnetism, nonlinear optics etc [2]. In the present study, we have constructed four new Cd(II) coordination polymers (CPs), formulated as $[Cd(L1)(Formamide)_2]_n$ (**1**) and $[Cd_2(L2)_2(MeOH)_2]_n$ (**2**), $[Cd_4(L1)_4(DMF)_6]_n.3n(DMF)$ (**3**) and $[Cd_2(L2)_2(DMF)_3]_n.2n(DMF)$ (**4**), using the polyaromatic group-containing carboxylic acid pro-ligands 5-{(anthracen-9-ylmethyl)amino}isophthalic acid (H_2L1) and 5-{(pyren-1-ylmethyl)amino}isophthalic acid (H_2L2) and cadmium nitrate under solvothermal conditions. The CPs **1** and **2** were used for the adsorption of various cationic and anionic organic dyes in aqueous medium, which was monitored by UV-Vis spectroscopy. Both CPs are highly effective for the removal of cationic dyes in comparison to anionic ones. However, the two-dimensional pyrene group containing CP **2** shows a higher efficiency (removal efficiency of 75-97%) in removing three cationic dyes [3]. The adsorption kinetic and adsorption isotherms of these CPs were also determined. However, the CPs **3** and **4** display efficient catalytic activity towards solvent-free Strecker-type cyanation reactions of different acetals, with trimethylsilyl cyanide (TMSCN). CP **3** is more effective (yield 96% within 4 h of reaction time) than CP **4**. The recyclability tests show that the CP **3** can be recycled at least five times without a marked decrease of its catalytic activity [4].

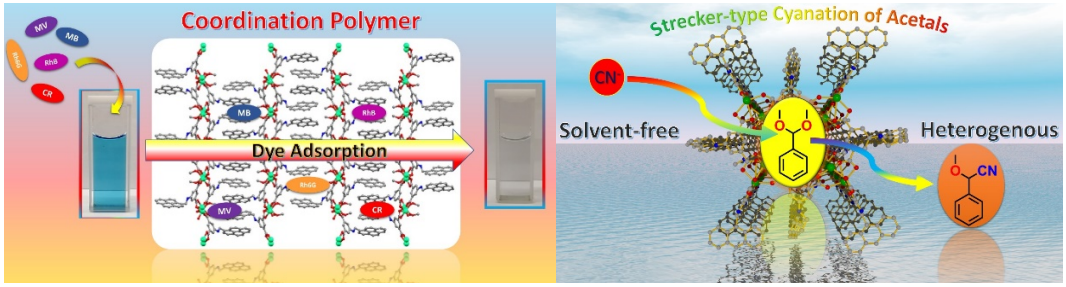

Figure 1. Organic dyes removal and catalytic applications of Cd(II) coordination polymers.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A. Karmakar express his gratitude to IST and FCT for Scientific Employment contract (Contrato No: IST-ID/107/2018) under Decree-Law no. 57/2016, of August 29.

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P37

Ethylene photooxidation using BEA zeolite based TiO_2 composites

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Ethylene is a natural hormone for the maturation process of climacteric fruits and is released during the respiration of fruits. The maturation process decreases fruit shelf-life, increasing the waste production [1]. An efficient and cheap process to control and remove ethylene consists in decomposing it into CO_2 and H_2O in the presence of a photocatalyst (i.e. a semiconductor under light irradiation). The most common semiconductor used in photocatalysis is TiO_2, due to its high efficiency and low cost. However, the use of bulk TiO_2 has a few drawbacks, such as a limited adsorption for reactants and products [2]. One way to overcome this limitation is to support TiO_2 onto zeolites as they present high surface area and high adsorption capacity that allow to gather and easily concentrate reactants. In particular, BEA zeolite, a highly hydrophilic material with a high external surface area, seems to be a very good candidate to support TiO_2 nanoparticles.

TiO_2/BEA composites (BEA from Zeolyst with a Si/Al ratio of 12.5) were prepared by sol-gel method, using two different alcohol solvents (2-propanol and ethanol). The use of two different solvents allowed to obtain composites with slightly different features that impact on the ethylene photooxidation. For both solvents, composites with two different TiO_2 concentrations were prepared (20 and 30 % wt.) and compared. Ethylene photooxidation was performed with a fixed bed quartz reactor, loaded with 0.45 g of catalyst with a gas mixture containing C_2H_4/He/N_2/O_2. The initial ethylene concentration was 100 ppm. Before every reaction the gas was let to pass in the reactor to reach the adsorption-desorption equilibrium (dark experiments). After that, the reactor was irradiated by a medium-pressure mercury lamp (125 W). The lamp is placed in a quartz or glass water cooling jacket, for experiments under UV-Vis or UVA-Vis range ($\lambda > 350$ nm), respectively.
DRS UV-Visible spectroscopy was performed and showed that all samples absorb light below 350 nm. XRD characterization was also performed and revealed that TiO_2 anatase phase was present in all composites, but particles size was different between each method: larger particles size when 2-propanol is used and smaller ones for ethanol solvent.

Ethylene photooxidation results showed that: i) samples present higher conversions under UV-Vis irradiation than under UVA-Vis irradiation, since TiO_2 could absorb more light and generate more radicals, ii) samples prepared with ethanol had higher ethylene conversions than those prepared with 2-propanol, probably because a higher dispersion of TiO_2 particles in the zeolite matrix is obtained for method 2, and iii) sample with 30 % TiO_2 (ethanol as solvent) reached 100 % ethylene degradation, converting all ethylene into CO_2 and H_2O under UV-Vis irradiation.

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P38

Light propelled nanovehicles for drug delivery

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In recent years, the interest in nanocarriers for controlled and intelligent cargo delivery systems has increased due to their versatility and promising applications. These can already address very well-defined morphology, large cargo capacities, targeting of the destination, and on-demand controlled delivery. [1-6]

The goal of this project was to add self-propulsion capabilities to these nanovehicles, transforming them in versatile nanorobotic tools. Our proof-of-concept nanovehicles are Janus nanoparticles (JNPs) composed by a silica core and a gold nanostructure in half of their surface. Upon irradiation, the vehicle is propelled in the opposite direction of the gold half-shell by the photothermal effect.

Janus Nanoparticles are produced by a high yield process based on microparticle templating, specifically via a Pickering emulsion route. The optical properties of the Janus nanoparticles, in particular their plasmon resonance, can be tuned by varying the gold nanoshell thickness. The motion of the nanovehicle was evaluated to determine the diffusion regimes upon irradiation.

Our proof-of-concept system exhibited a strong plasmon optical resonance. Upon irradiation with a 632.8 nm laser, it showed the occurrence of two diffusion regimes: translational and rotational. The average directional velocity reached by this system was 3.95 μm/s.

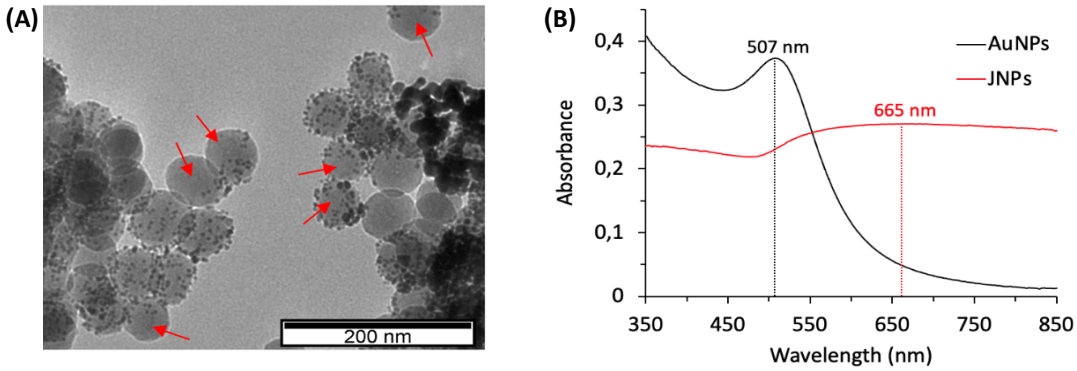

Figure 1. (A) TEM image of JNPs (scale bar: 200 nm). (B) Absorption spectra of gold nanoparticles (AuNPs) and JNPs.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P39

Advanced High Strength Steel in sodium chloride media: corrosion characterization

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This study aims to investigate the corrosion behavior of Advanced High-Strength Steels (AHSS) in sodium chloride media (NaCl), emulating marine environments and acidic rain during vehicle use-phase. Steel is the most relevant material in structural applications due to its cost-effectiveness [1]. Lightweighting, safety and cathodic protection are sought for vehicle structure application, and currently only galvanized press-hardened steel (PHS GI) is expected to fit those demands [2].

In this study, PHS with different GI coatings PHS with aluminum silica (AlSi) coating, and complex phase (CP) steel with GI coating were considered. Corrosion resistance of the coated steels was studied using electrochemical impedance spectroscopy (EIS) and d.c. polarization. The corrosion behavior at microscale was studied employing localized electrochemical techniques – scanning vibrating electrode technique (SVET) and scanning ion-selective electrode technique (SIET). The media used were 1.6 M NaCl neutral pH, 0.05 M NaCl neutral pH, and 0.05 M NaCl pH 3. Optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy were used to disclose the complementary information on corrosion products distribution and composition. Protective ability of the corrosion products was evaluated in different electrolytes.

In 1.6 M NaCl neutral pH media, PHS GI exhibited a higher corrosion rate at early stages that could be reduced over time with a diminution of the active area. PHS AlSi had significantly less sacrificial behavior compared to PHS GI. CP presented a corrosion behavior determined by galvanic coupling between zinc coating and the steel substrate. This steel demonstrated lower corrosion rate, higher sacrificial behavior, and higher stability of the corrosion process due to the formation of a relatively uniform layer of corrosion products.

Remarkable differences were detected and studied during corrosion in 0.05 M NaCl pH 3: PHS GI underwent less degradation, while providing considerable cathodic protection compared to CP.

Therefore, PHS GI can be a viable alternative to CP steels and GI coatings, and may achieve superior cathodic protection to AlSi, providing appropriate corrosion protection for vehicle structures.

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This research work has been implemented within the framework of the European project AtHyCor “Modelling of hydrogen activity from atmospheric corrosion in ultra-high strength steels for light structure application”. This project has received funding from the Research Fund for Coal and Steel under grant agreement No 101034041.

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P40

Pollutant Recycling and Remediation using High-Performance Carbon-based Composite Materials

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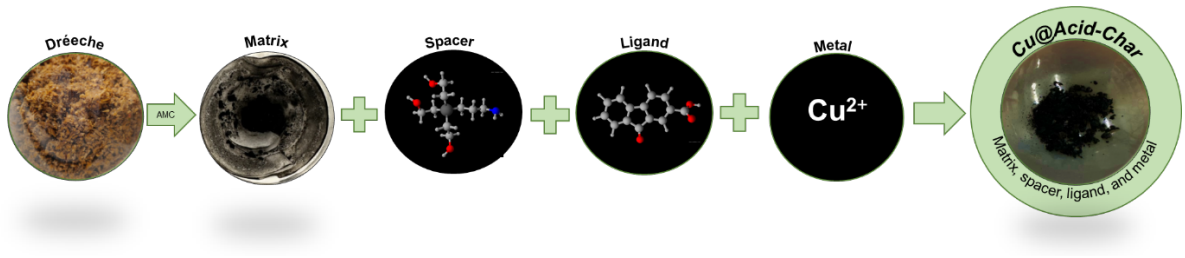
Water is essential for life, human health, economic and social growth. As the world's population grows, so does the demand for water. The increased use of pharmaceutical and personal care products (PPCPs) has contributed to the contamination of water systems, thus motivating the development of new techniques to deal with this problem [1-3].

The current work aims preparing the unique carbon-based composites for pollutant remediation in aqueous systems. The preparation of composites encompasses the valorisation of waste and renewable feedstock, followed by the use of composites in treatment of contaminated water, as well as to construct lab-validated technology with increased circular and sustainability properties. The carbon-based were generated via an acid - mediated carbonization (AMC) of brewer's spent grain (dréeche). The surface of acid-chars was functionalised with a bottom-up methodology (matrix, spacer, ligand, and metal) to give the final composite products.

In our design we used (3-aminopropyl)triethoxysilane as a spacer, 9-fluorenone-2-carboxylic as an ligand, and copper(II) nitrate as a metal source (Scheme 1). The obtained carbon-based materials were fully characterized by FTIR, elemental analysis, solid-state NMR, SEM, XPS, and PXRD methods.

The degradation and remediation of model PPCPs are currently being tested with these new carbon-based composites by exploring both the catalytic degradation and selective sorption approaches. The use of brewer's spent grain as a feedstock represents an effective strategy to generate unique self-standing carbon-based composites for PPCPs degradation, with a particular relevance to sustainable chemistry and environmental catalysis.



Scheme 1

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P41

9-Borafluoren-9-yl and diphenylboron tetracoordinate complexes of 8-quinolinato ligands with heavy atom substituents: synthesis, fluorescence and application in OLED devices

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In order to accomplish great light emissions and, consequently, Organic Light-Emitting Diodes (OLEDs) with higher efficiencies it is crucial to take advantage of the triplet states of the molecules. When it comes to an electrical excitation process, the charge carrier recombination, according to statistics, generates only 25% of singlet states while the remaining 75% are triplet states [1]. Hence, it is crucial that the emitting materials own appropriate electrical and optical properties to completely use the singlet and triplet excitons for energy conversion. It is possible to enhance the singlet exciton formation with delayed fluorescence (DF), being the two principal acknowledged mechanisms of this process the triplet-triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF) [2]. Following our very recent publication [3] of new four-coordinate tetrahedral boron complexes, containing 9-borafluoren-9-yl and diphenylboron cores attached to orthogonal F- and Cl-substituted 8-quinolinolato ligand chromophores that have shown DF intensity originated from TTA, we report now analogue compounds with heavy atom substituents with the goal to enhance the generation of triplet states. Herein, its photophysical properties regarding the mechanism governing the DF and its application in OLED devices will be discussed.

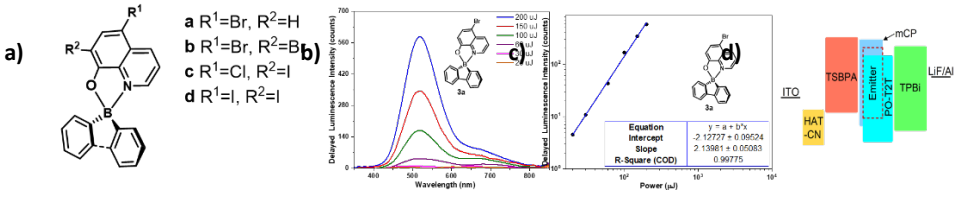

Figure 1. 9-borafluoren-9-yl and diphenylboron compounds (a), dependence of DF intensity on the excitation dose (b), log-log plot of DF intensity as a function of excitation dose (c), and structure of an OLED device (d).

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P42

Triamcinolone acetonide delivery from cyclodextrin-containing contact lenses to treat diabetic retinopathy

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The prevalence of diabetic eye disease is continuously rising worldwide and encompasses a variety of ocular conditions such as diabetic retinopathy (DR), macular oedema, and glaucoma [1]. Triamcinolone acetonide (TA) is the most common corticosteroid used in the management of DR and is administered intravitreally. Despite being the most efficient route to deliver the drug to the posterior part of the eye, it may induce severe ocular complications [2]. Contact lenses (CL) constitute an advantageous platform for the topical release of ophthalmic drugs by providing prolonged levels in tear fluid [3]. However, the lack of interaction between CLs and lipophilic steroids hampers its ability to load therapeutic amounts.

Herein, we incorporate cyclodextrins (CDs), cyclic oligosaccharides with lipophilic cavities, to improve drug loading and release from CLs [4]. Two approaches were evaluated: grafting of CDs to preformed hydrogels (g-CD) and the addition of CDs to the monomer's solution before polymerisation (i-CD). The effect of the CDs on the hydrogel's properties, namely in solvent uptake, transmittance, and stiffness, was studied. Moreover, the effect of sterilisation by high hydrostatic pressure (HHP) was assessed. TA was loaded by soaking in a drug suspension (0.3 mg/mL). The drug-loaded hydrogels were used for *in vitro* drug release tests in sink conditions and biocompatibility assays. Finally, the anti-inflammatory activity was investigated.

The designed hydrogels revealed physical properties suitable for CLs. Functionalisation with CDs endowed the hydrogels with a stronger affinity for TA and sustained release for several days. i-CD CLs doubled the affinity of TA to the network and resulted in the highest amount loaded (10 mg/g dry lens). Cytotoxicity in human corneal epithelial cell cultures and HET-CAM tests confirmed the safety of the therapeutic CLs. TA released from the CLs decreased the secretion of pro-inflammatory cytokines. Overall, the CLs were revealed to be suitable candidates for the topical ocular application of TA.

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P43

On the Stability of Celecoxibe-Tramadol·HCl: Co-crystal versus Amorphous Nanoparticles

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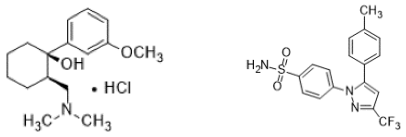
Co-crystal technology has gained considerable traction in recent years due to its potential to create novel materials and improve the properties of existing ones. Recently a new co-crystal combining the active pharmaceutical principles (Figure 1) tramadol hydrochloride (THC, used to treat moderate to severe pain) and celecoxib (CEL, an anti-inflammatory drug) was reported, that presented favorable physicochemical properties and dissolution profiles for application in dual therapy [1]. This led us to consider if an identical API combination can be formulated as a co-amorphous form, given the potential advantage offered in terms of solubility and dissolution rate enhancement.

A critical aspect within this context is the accurate assessment of: (*i*) the stabilities of co-crystal versus co-amorphous forms; (*ii*) the stabilities of the different forms relative decomposition into the individual precursors. Indeed, both the transformation of an amorphous into a crystalline form or the decomposition of any form of the binary compound into the precursors can have a dramatic effect in the bioavailability and shelf life of a drug [2].

Recent evidence seems to point out that co-crystal stability is, most often, enthalpically controlled, reflecting a lattice energy advantage associated with the combination of the individual precursors in a single crystal lattice [3]. Thus, in this work the two types of stability mentioned above were evaluated for different THC:CEL (co-crystal and co-amorphous nanoparticles of different particle sizes). The assessment was based on the determination of the standard molar enthalpy of the dissociation reaction, $\Delta_r H_m^o(1)$:

$$\text{THC:CEL(cr/am)} \rightarrow \text{THC(cr)} + \text{CEL(cr)} \qquad (1)$$

from solution calorimetry measurements. The results unequivocally indicate that the stability of THC:CEL increases as the material becomes more crystalline and the particle size increases. This is consistent with the observation that the amorphous forms evolve into the crystalline form overtime.



(a) (b)

Figure 1. Molecular structures of (a) tramadol hydrochloride (THC) and (b) celecoxib (CEL).

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P44

Polydopamine/polypyrrole co-polymers for amperometric biosensors

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The combination of amine and catechol groups provides interesting adhesive properties to polydopamine (PDA), a biomimetic polymer inspired by the mussel's foot proteins. This versatile polymer allows the coating and functionalization of practically all types of surfaces, having great application in several areas, such as biomedicine, nanotechnology, and (bio)sensing [1,2]. However, PDA is a chemically heterogeneous and poorly conductive polymer, which limits its electrochemical utility, including its use in amperometric biosensors [3,4]. To overcome this limitation, this work aims to optimize and explore the electro-co-polymerization of two monomers, dopamine (DA) and pyrrole (Py); the latter known to origin a highly electronically conducting polymer – polypyrrole (PPy). The combination of PDA's adhesivity, for further functionalization (*e.g.*, biomolecules) with the high conductivity of PPy, useful in electron transfer events, in a single polymer is expected to have an exceptional impact on the use of polycatecholamines in biosensing interfaces and electrocatalytic applications.

Hereby, we have fully characterized potentiodynamic and potentiostatically grown co-polymers (PDA/PPy), regarding their electrochemical behavior, optical properties, thickness, morphology and wettability, by using a combination of electrochemical and surface characterization techniques (ellipsometry, electrochemical quartz crystal microbalance, atomic force microscopy, water contact angle measurements and FTIR). Overall, the co-polymers, *ca.* 30 nm thick, revealed superior electrochemical response towards both negatively and positively charged ionic probes, as well as towards target phenolic compounds, regarding pure polycatecholamine films.

Real-time surface plasmon resonance was employed to confirm the robust immobilization of a laccase enzyme on the co-polymer functional groups, aiming at preparing the biosensor interface. Chronoamperometric assays of the laccase-modified co-polymer electrode were successfully evaluated for the sensitive detection of gallic acid (a model phenolic compound). The catalytic properties of these adhesive and conducting matrices were greatly improved regarding pristine PDA thin films.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. L. C. Almeida acknowledges PhD scholarship SFRH/BD/ 129566/2017, COVID/BD/152149/2022.

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P45

Niacin Crystal Nucleation from Ethanol Solutions

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Crystallization is one of the most used methods to obtain pure solids from a solution. Although used since ancient times, there are still many questions regarding how this process occurs, especially on a molecular level. Nucleation, the first step in the crystallization process, corresponds to the aggregation of molecules in solution to form nuclei, which grow into crystals. This step plays an important role in determining the properties of the crystalline material, namely the crystal habit, particle size distribution, and molecular arrangement in the solid state [1]. A broader knowledge of these phenomena would allow for tighter control of the physical properties of the produced materials, preventing, for example, the synthesis of undesired crystal phases. This has been the origin of several serious problems recorded in the pharmaceutical industry during the manufacturing process of drugs (e.g., Norvir) [2]. As such, the present work seeks to provide insight into the nucleation events that occur in solution and that lead to the genesis of a crystal.

Niacin (Figure 1), a pharmaceutical drug with applications, e.g., in the regulation of cholesterol levels, was chosen to investigate the initial stages of the crystallization process from solution. Three different methods were used: (i) Differential scanning microcalorimetry (μDSC) (ii) Measurement of crystallization induction times (iii) Molecular dynamics (MD) simulations. In brief, it was found that the nucleation process of this compound cannot be described by using the classical nucleation theories and it seems to exist a relation between the crystallization mechanism and the supersaturation level and the initial concentration of the solutions.

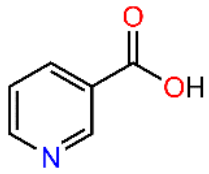

Figure 1. Chemical structure of niacin.

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P46

Removal of Dyes from Aqueous Solutions using Poly(ionic liquid)s

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Dyes are believed to have been used over 180,000 years ago, mostly extracted from plants, but nowadays more than 1 million tons are industrially produced each year and used primarily by textile industries [1]. In these industries, for the textile dyeing process, the dye is hydrolysed. As a result, about 10 to 15% of the dye used remains unused and discharged into the environmental [2]. This causes problems to the aquatic life and therefore industrial wastewater treatment needs to be performed before releasing. Poly(ionic liquid)s (PILs) have already been explored as adsorbents for the extraction of acid, basic and azo dyes such as bromo phenyl blue, methyl blue, orange II, sunset yellow or amaranth, mainly through the use of imidazolium based PILs [3-4].

The purpose of this study is to assess the true potential of PILs, specifically powder of poly(diallyldimethylammonium NTf2), as sorbent materials for removing direct red 80 dye and

reactive blue dye from aqueous solution, using a thermomixer.

Furthermore, the optimization of extraction parameters such as time, initial dye concentration, ratio of PIL to aqueous solution and PIL particle size were evaluated. Analysis of dye removal efficiency was performed with a UV-vis spectrophotometer (Shimadzu UV Spectrophotometer).

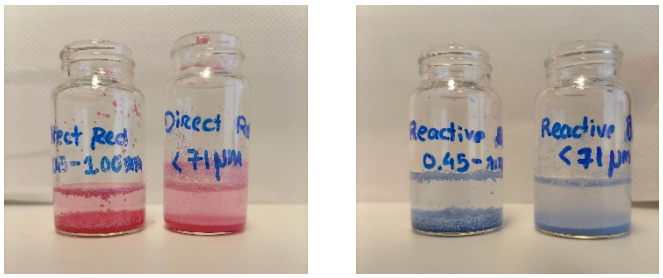

Figure 1. Direct red 80 dye and reactive blue dye solutions after PIL's extractions.

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P47

Revisiting the vapor liquid equilibria of water+methanol and ethanol+n-butanol binary mixtures

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The interest in mixtures of alcohols and water has increased due to its relevance to refinery industries. These compounds can be added to gasoline enhancing the octane number, improving combustion, and reducing emissions. [1]

The typical technique applied to produce bio-butanol is the acetone-butanol-ethanol (ABE) fermentation from biomass. The produced butanol needs to be separated from acetone, ethanol, and water. This separation must be as efficient as possible to maximize the amount of recovered butanol. To optimize this process, for design new distillation columns, for modelling separation processes on different stages of development, and for revamping of existing chemical plants, accurate and thermodynamically consistent vapor-liquid equilibrium data is needed. [1-3]

In this work vapor-liquid equilibrium data at high temperatures for the binary mixtures (methanol+water and ethanol+butanol) will be revisited with the purpose of evaluating the accuracy of the existing data. The importance of such systems will be discussed and new data will be provided.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P48

On the Hydrophobicity of Hydrophobic Eutectic Solvents

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Separation procedures are fundamental in a vast array of industries such as pharmaceuticals, biorefinery and petrochemistry. In this field liquid-liquid extraction is a very appealing technique due to its high efficiency, selectivity, robustness, flexibility and easiness of operation [1]. Simple procedures using volatile organic solvents (VOCs) and aqueous solutions were employed for many decades to perform extractions and separations. However, alternative solvents such as thermotropic systems, switchable solvents and aqueous two-phase systems have been slowly emerging. More recently, ionic liquids and eutectic solvents started to replace conventional VOCs due to their lower vapor pressure and toxicity. Additionally, the capacity to design task specific solvents led to high specificity and process efficiency. The use of these solvents enabled to widen the properties of alternative solvents and shift from the very interesting aqueous biphasic systems to a more hydrophobic domain [2,3].

In this work, binary one phase mixtures of n-hexane and hydrophobic ES, D,L-menthol:dodecanoic acid (2:1), were separated by adding low molecular glycols (ethylene glycol, diethylene glycol, triethylene glycol, PEG 200, PEG 400, PEG 600). The liquid-liquid phase equilibria diagram of these 6 ternary systems was measured through the turbidimetry method and 3 tie-lines for each system were determined by GC-FID, allowing to conclude about the ESs stability. Finally, these systems were used to extract carotenoids and chlorophyll from microalgae (Spirulina and Chlorella).

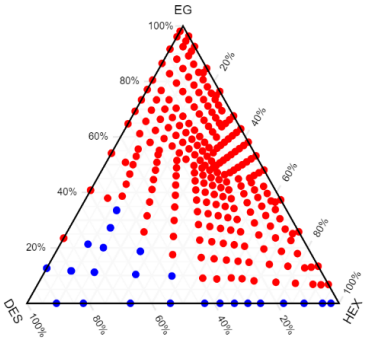

Figure 1. Simplified liquid-liquid phase equilibria diagram (in molar percentage) for the ethylene glycol, hexane and D,L-menthol:dodecanoic acid (2:1) system. Monophasic behavior (blue) and biphasic behavior (red).

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Afonso J. gratefully acknowledges the financial support of FCT/MCTES (Portugal) for PhD fellowship 2021.07949.BD and the CQE project PTDC/EAM-AMB/2023/2021.

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P49

Influence of mechanochemical treatments on the structural and textural properties of zeolites

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Zeolites are inorganic materials with a wide range of applications as adsorbent and heterogeneous catalysts. However, for some applications the particle size and texture need to be tailored [1,2]. In this work BEA and ZSM-5 zeolites were modified through mechanochemical treatments in a shaker mill (VWR star-Beater) using five 3 mm steel balls, changing time and frequency. The samples were labeled as ZEO_*F*_*t*, where *F* is the frequency (Hz) and *t* is the milling time (min). To evaluate the impact of mechanochemical treatments on the materials properties, parent and modified zeolites were characterized by powder X-ray diffraction, low temperature N_2 adsorption isotherms and light scattering experiments. Figure 1 shows the volume density profiles as a function of particle size distribution and Table 1 displays the crystallinity, textural parameters, and mean particle size.

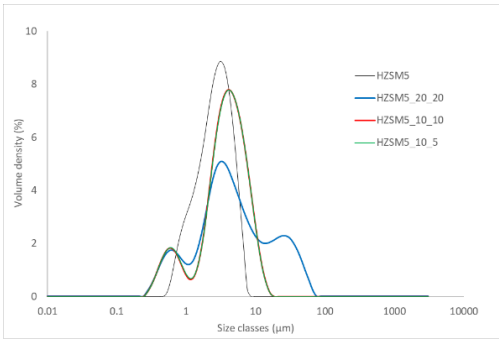

Figure 1. Particle size distribution for ZSM5 series.

Table 1. Crystallinity degree (C_{XRD}) micro and mesoporous volumes (V_{micro} and V_{meso}) and mean particle size (D_{50}).

Sample	C_{XRD} (%)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	D_{50} (µm)
HZSM5	100	0.15	0.22	3.51
HZSM5_20_20	88	0.11	0.08	5.6
HZSM5_10_10	95	0.14	0.07	4.04
HZSM5_10_5	96	0.15	0.07	4.07
HBEA	100	0.13	0.40	7.65
HBEA_20_20	56	0.08	0.30	9.68
HBEA_10_10	87	0.15	0.41	8.63
HBEA_10_5	74	0.14	0.41	8.76

Preliminary results show that more severe treatments (e.g high milling frequencies of 20 Hz) result in some loss of crystallinity and decrease on the textural parameters. Also, the presence of bulky crystal aggregates is noticed. For lower frequencies (10 Hz) the effect of milling time does not affect V_{micro} and, in both cases presented in Figure 1, the presence of smaller aggregates than those detected in the starting material is observed.

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What about Butanol?

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For several years alcohols have been considered as one of the possible renewable solutions for the transportation sector. Many studies have been conducted with alcohols such as methanol, ethanol, butanol[1][2]. Due to its larger similarity to gasoline, longer hydrocarbon chain, lower oxygen content, higher heating value when compared to methanol and ethanol and the high tolerance to water contamination which permits the use of the existing distribution pipelines, butanol has been pointed as a promising fuel candidate [3]. However, there are still questions to be answered so it can be used as additive or drop-in fuel.

In this work, several properties of biodiesel+butanol+ethanol blends were studied and compared with existing studies in order to better understand its behavior in the search for new answers. Advantages and disadvantages were observed in such blends, and the best blends were pointed out for the continuance of the study.

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SUSeeds: Sustainable Biopolymer-based Coatings for Seeds

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Seeds constitute the most dynamic frontier of technological development in the agricultural area, being direct and indirect depositaries of a large part of technological advances. Seed coating plays a crucial role in promoting sustainable agriculture by providing protection to seeds and seedlings from pests and diseases and ensuring uniform support in a wide range of soil types, cultural practices, and environmental conditions [1]. In this context, our SUSeeds project focuses on the design of new films or multifunctional capsules based on biodegradable biopolymers to coat the surface of different types of seeds.

The use of biopolymers as a coating or adhesive component in seeds has proved to be important in different aspects such as gain in robustness, minimization of seed damage and improved handling [2]. The biopolymeric material can be used in conjunction with other components, thus adding to the physical protection an additional biological protection perspective such as an antimicrobial action [3].

The main objectives of this project are: (1) the preparation of multifunctional formulations and coatings based on biodegradable biopolymers using film coating and encapsulation techniques; (2) the physicochemical, mechanical and biological characterization of the coatings; (3) the production of coated soybean and corn seeds, the preparation of encapsulated tomato seeds, and the germination and vigor tests of the obtained seeds; (4) risk management, coatings optimization and the assessment of sustainability indicators.

The SUSeeds project is totally aligned with several challenges of the UN 2030 Agenda for Sustainable Development, and it is expected that new biodegradable multifunctional formulations and derived materials can be rationally designed for applications in sustainable chemistry and seed industry. This presentation will showcase the main results already achieved in our laboratories on the use of biopolymer-based formulations for seed coating.

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Nanostructured Coatings for Heritage Stone Surfaces

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Stone materials are one of the most used materials in the history of mankind being limestone one of the stones that is more used in cultural heritage sites in Portugal. However, stone can suffer deterioration by both natural and/or anthropogenic causes and limestone is one of the stones that is more prone to such deterioration, namely by the contact between water and the surface of the stone. The goal of this work is to tackle this problem by creating nanostructured functional coatings that resist water and that have stain repellency properties. This surface treatment should be easily scaled-up, resistant to wear and maintain the original appearance of the natural stone. This can be done by using Silica Nanoparticles in order to create surface roughness and consequently induce superhydrophobic properties onto the stone. Nanoparticles of ca. 50 nm diameter were functionalized with groups that increase the interaction with the stone surface. A schematic of the coating can be seen in Figure 1. These functional stone coatings will impart novel high-performance features to limestone having the potential to help the industry by increasing the value of the natural stone while using “green technology” because of the reduced environmental impact, low energy cost and biocompatibility.

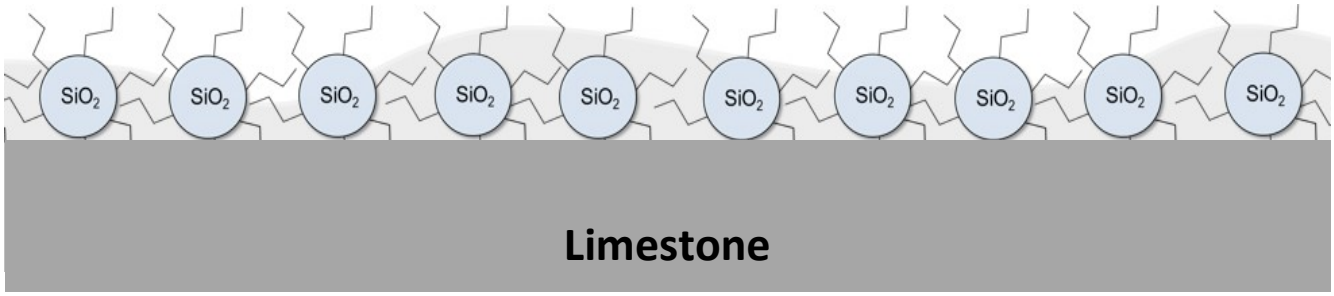

Figure 1. Limestone coated with the dispersion of functionalized silica nanoparticles in a hybrid silica matrix.

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Does particle size matter? Performance of pine nut shell-derived PACs in improved drinking water treatment technologies

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Activated carbon adsorption is considered one of the best available technologies to tackle the presence of microcontaminants in natural waters, e.g., pharmaceutical compounds (PhCs), natural organic matter (NOM) and cyanotoxins (naturally produced by cyanobacteria in drinking water source reservoirs), that are resistant to conventional treatments [1]. The development of advanced drinking water treatment (DWT) processes calls for high-performing powdered activated carbons (PACs), as those prepared in this work by physical (steam or CO_2) activation of carbonized pine nut shells (PNS, a by-product of the food industry) with particles below 150 µm diameter [2]. Different fractions of lab-made PACs, S2 and C3, and of the commercial PAC, NORIT SAUF, were obtained by sieving and particle size distribution was assessed by SEM (Figure 1) and laser diffraction spectrometry. Each fraction was characterized regarding textural properties (with smaller particle sizes generally being associated with higher total and mesopore volumes), density, moisture content and pH_{PZC}. With previous studies highlighting the excellent adsorption capacity of lab-made PNS PACs for the removal of three PhCs from spiked real wastewater [2], fractions < 20 µm and 20-75 µm are being tested in dechlorinated tap water for the adsorption of spiked PhCs and NOM surrogate compounds. Smaller particle sizes will, in principle, allow faster kinetics and ideally, higher adsorption capacity, but may hinder the particle retention in conventional DWT. These materials will be further applied in coagulation/flocculation/sedimentation (20-75 µm), for conventional DWT processes, and with membranes (< 20 µm), as a hybrid adsorption-membrane technology, for advanced DWT.

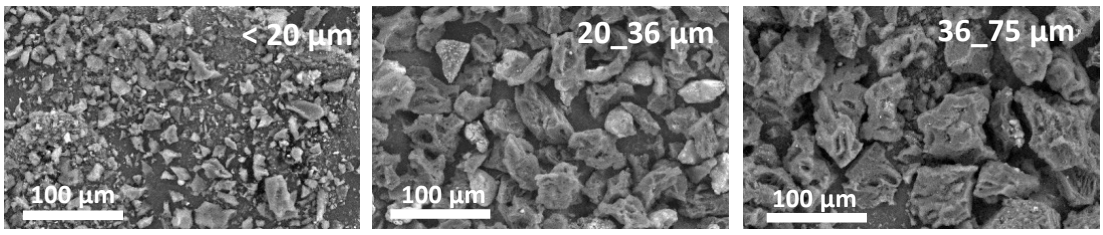

Figure 1. SEM images for different fractions of PNS-derived PAC S2.

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P54

Ultrasound-responsive hybrid nanocontainers for controlled release

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The side effects of a drug can be greatly decreased when it is delivered only in the needed location and in a timely manner. Nanoparticles, in particular Mesoporous Silica Nanoparticles (MSNs), are the ideal candidates to achieve that goal as they combine a large surface/volume ratio with a versatile surface modification. Their pores, with widths between 2-8 nm, are available for solvent diffusion, allowing the incorporation of different drugs. [1-4]

Ultrasounds are often used in clinical applications, and in the case of cancer treatment for ultrasound-guided biopsy or to ablate tumor tissues. Ultrasounds have several advantages over other techniques/equipment's since they are more affordable and easier to use when compared to magnetic resonance imaging or computerized tomography. By combining nano-systems with ultrasounds, specifically high-intensity focused ultrasound (HIFU), it might allow for a more localized cancer treatment at the tumor site as the nanoparticles can target tumors via passive or active targeting, and it can also improve the sensitivity of tumor detection as it allows for a high-resolution ultrasound imaging. [5]

In this project the objective is to produce hybrid MSNs with *ca.* 50 nm diameter and pores of 3 nm diameter, incorporating disulfide bonds within the silica network and present the response of these nanoparticles by the effects of ultrasound activation, such as HIFU. The strategy relies on the low bound-energy of the disulfide group that are sensitive to ultrasounds frequency and is expected to break under those condition and release the MSN cargo in a rapid and efficient way.

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P55

Engineering ZnO nanoparticulate system with Se for medical application

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To deal with the rapidly growing bacterial resistance, new antibacterial substitutes with high and enduring activity are urgently needed. Zinc oxide (ZnO) nanoparticles (NPs) have been extensively studied for their antibacterial properties due to their ability to generate reactive oxygen species (ROS) that can damage bacterial membranes and DNA . The addition of selenium (Se) to ZnO NPs can further enhance their antibacterial activity, as this is an element also known to have antimicrobial properties. Moreover, the osteoinductive activity of ZnO, allied to Se, an essential trace element in humans closely linked to bone health, can promote bone tissue regeneration [1, 3, 4].

Therefore, developing selenium-doped zinc oxide (Se-ZnO) NPs not only offers a potential solution to the problem of bacterial resistance but has also the potential to promote bone tissue regeneration.

As such this work focused on the conventional synthesis of selenium-doped zinc oxide (Se-ZnO) NPs with different Se contents. The obtained NPs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared (FT-IR) analyses. The as-synthesized Se-ZnO NPs showed a round-shaped morphology with average sizes of 100 nm. The addition of Se atoms has not modified the ZnO lattice, as confirmed by XRD, and the characteristic bands of ZnO are preserved in FTIR spectra.

Overall, our study as shown that simple and low-cost methods can be used to synthesize Se-ZnO NPs, which have the potential to be utilized as both antibacterial agents and bone-regenerative biomaterials.

Keywords: ZnO nanoparticles; Selenium; Se-ZnO; Antibacterial activity; bone tissue regeneration

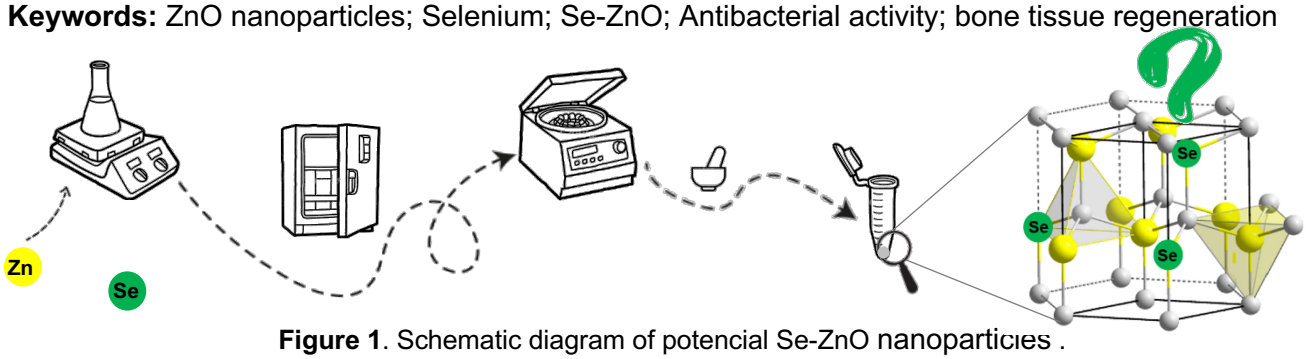

Figure 1. Schematic diagram of potencial Se-ZnO nanoparticles .

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Purine sensing with metal-organic framework films

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Uric acid is a molecule with a high role in medical applications since its abnormal concentration translates into a diagnosis of clinical diseases. Therefore, the development of purine sensors became extremely important and relies on the fabrication of thin films based on nanomaterials, like metal-organic frameworks. [1,3]

Metal-organic frameworks (MOFs) consist of organic linkers and a metal ion and have been intensively studied as catalysts, sensors and in molecular separation and storage due to their properties such as high porosity, crystallinity and the presence of several active sites. [2]

In our research, we focused on Fe-MOF-74 and on the development of films using a direct electrochemical deposition technique - cathodic deposition - that uses the MOF precursors directly.

To produce the films, we used two different organic linkers, one of them commercially available and the other one was synthetised and characterised by nuclear magnetic resonance spectroscopy.

The films obtained were characterised by diffuse reflectance infrared fourier transform spectroscopy (DRIFT), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The new films were used for the electrochemical sensing of uric acid.

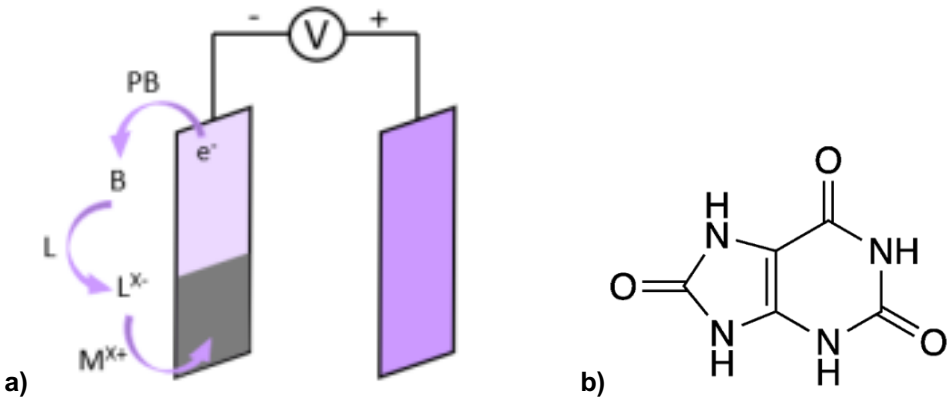

Figure 1. (a) Electrochemical MOF film fabrication method, cathodic deposition. (b) Uric acid, molecule used as the analyte in the electrochemical sensing experiments.

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Energetic Ionic Liquids As Additives In High-Energy-Density (Hed) Fuels

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Nowadays, hydrazine and its derivatives are frequently used as bipropellants. However, because of its high toxicity and instability, it's based-fuels are extremely risky to handle and store. As a result, researchers have been exploring "greener" alternatives. Recently, a new class of high-energy density (HED) hypergolic fuels have been emerging using energetic ionic liquids, due to their unique physical and chemical features such as low vapor pressure, high thermal and chemical stability and good electrical conductivity. Studies have been conducted based on ionic liquid and biofuels blends in different volume proportion [1]–[3]. In this work these studies will be critically reviewed and their capability of being a promising replacement to the currently used toxic fuels will be evaluated.

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Diatomaceous Earth as Functional Filler for BioPolyurethane Coatings

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Polyurethanes (PUs) are becoming increasingly important materials for protection of surfaces. PU characteristics, such as superior adhesion, good mechanical strength, chemical resistance, and weathering stability, make it a suitable and widely used polymer for corrosion protection of steel. Usually produced by the polymerization reaction of polyisocyanates with polyhydric alcohols, the synthesis often utilizes petroleum-based raw materials, not complying with modern standards of sustainability and green chemistry. The development of biopolyurethane (BioPU) chemistries, with the utilization of biomass-based polyols, allows for the possibility to impart new functionalities to PU coatings, while alleviating the dependency on fossil-fuel feedstocks [1,2].

For the formulation of polymeric coatings, it is common to add fillers in order to improve specific properties and the composite performance. Many inorganic particle fillers, such as titanium dioxide, zinc, and silica, have been shown to improve the composites characteristics, such as hardness, abrasion resistance, weathering and UV resistance and enhanced corrosion protection [2,3].

Silica particles have been reported as fillers for polymeric composite coatings and generally the results show enhanced performance [3,4]. Among them, bio-derived diatomaceous earth (DE), also used as coating fillers, are extremely promising. These silica based, natural particles are the fossilized remains of microalgae, and have been used to impart super-hydrophobicity to organic coatings [5], as well as to carry high loadings of corrosion inhibitors in their silica cages [6].

In the current work, DE particles were added as a functional filler and corrosion inhibitor carrier, in a BioPU coating, developed from biomass derived polyols and a bio-based isocyanate. The characteristics of the BioPU composite coatings were analyzed (e.g., adhesion, hydrophobicity, thermal resistance, and barrier properties for corrosion protection). The results demonstrate that this biobased composite coating confers very promising corrosion protection properties.

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Smart self-sensing strategy for biobased polyurethane coatings

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Biobased polyurethane coatings for surface protection of steel components were developed based on the combination of bio-oil, obtained from biomass, and diisocyanate.

The bio-oil used to formulate the coatings was synthetized by liquefaction of pinewood sawdust with a moisture content of 10%. The pinewood was processed using the solvent 2-ethylhexanol and the catalyst p-toluene sulfonic acid [1]. The conversion of biomass into bio-oil reached 66,7% with an average recovery of the solvent of 78,3%. The bio-oil OH value was 188,6 $mg_{KOH}/g_{bio\text{-}oil}$.

During service coatings can be compromised and corrosion can develop and may be responsible for structural failures. Normally corrosion involves metal oxidation, oxygen reduction and also local pH changes. Thus, it's critical to identify coating deterioration and corrosion damage at the earliest possible stage [2]. For this reason, it's crucial to incorporate smart features into the coating formulation, namely pH responsive sensing molecules [3].

A rhodamine derivative compound was used as a pH sensing and corrosion sensing molecule. This molecule can be integrated into coating as a part of the polymeric chain or employing carriers/micro-particles. Since corrosion onset leads to pH changes, it enables detection of fluorescence above the active sites. This allows to detect the compromised zones, facilitating the timely maintenance of the structure and contributing to improved safety and sustainability.

Different biobased polyurethane coatings were produced and assessed by FTIR, fluorescence spectroscopy and electrochemical techniques. The developed coatings demonstrated innovative capability for corrosion detection and corrosion protection, simultaneously.

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New Optical Sensor for Boron Detection

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Boron can be beneficial to human health and agriculture in trace quantities, but becomes toxic to both humans and crops in excessive quantities [1]. Boron compounds are used in many industrial applications, including the fabrication of soaps and detergents, glass and ceramics, insecticides, fertilizers, semiconductors, flame retardants, high duress compounds, and active pharmaceutical ingredients. High boron contents in water might be the result of residual water discharges or leaching from rocks and soils containing borates and borosilicates [1].

Following our previous results using polyaromatic compounds with vicinal diols as boron sensors (based on 2,3,6,7,10,11-Hexahydroxytriphenylene) [2,3,4], in this work we have tested a fluorescent natural compound bearing aromatic vicinal diols as optical sensor for the detection of boron, in the form of phenylboronic acid, in aqueous media (Figure 1).

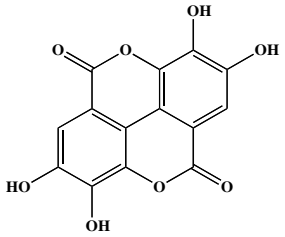

Figure 1. Structure of Ellagic Acid, here studied as a possible boron sensor.

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Gas Separation Performance of Fluorinated-based ILs Membranes under mixed gas conditions

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Gas separation is a significant and common industrial procedure used to remove impurities and undesirable substances from mixed gas streams, such as extracting carbon dioxide from other gases for carbon capture or separating hydrogen for use as a carbon-free transportation fuel. It is well known that using membranes to separate gas compounds is both economically more advantageous and significantly more effective than methods like distillation or absorption. For instance, and using the IL designer solvents properties, the best CO_2/N_2 separation performances among pure SILMs were attained by the [C_2mim][TFSAM] and [C_2mim][FSI] SILMs, that are on top of or beyond the Robeson 2008 upper bound, with CO_2 permeabilities of 753 and 843 Barrer and CO_2/N_2 permselectivities of 43.9 and 46.1, respectively [1]. However, the CO_2 separation properties of industrially relevant mixtures are often greatly changed by the presence of different gases in the mixture which result in limiting events, such as competitive sorption, penetrant-induced plasticization, or concentration polarization [2]. Although toxicity has been mainly linked to the cation and the length of its side chain, recent studies show that anions, especially fluorine containing anions, also contribute to their toxicity [3]. It is, thus, important to develop new fluorinated anions and test their CO_2 separation performance, in particular in the presence of other gases. In this work, the mixed gas permeation properties of SILMs using pure ILs bearing the [C_2mim]+ cation and various unconventional anions still bearing fluorinated moieties, such as [TFSAM], [FSI], [$C_4F_9SO_3$], [FAP], [BETI], and [TFSI], are presented. Industrially relevant CO_2 containing gas pairs , such as CO_2/N_2, CO_2/H_2, and CO_2/CH_4 in several compositions, are discussed and compared with those of single gas permeation properties.

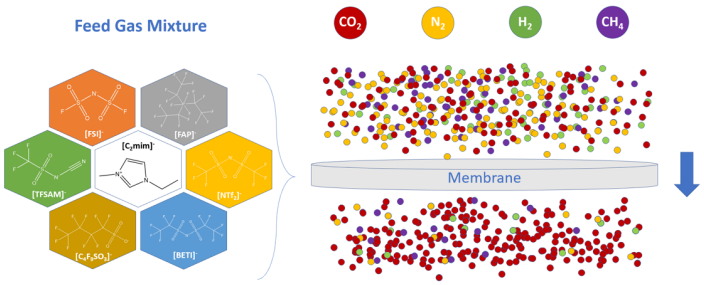

Figure 1. Liquid-Liquid phase equilibria diagram for water and IL ([C_2mim][F_3CBF_3]) as a function of ILs mole fraction. The lines are just to guide the eye.

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Kohlrausch–Williams–Watts Relaxation in Concentrated Sulfolane-$LiBF_4$ Mixtures

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Lithium-ion batteries (LIB) have become ubiquitous energy storage devices because of its advantageous qualities over its predecessors since its inception 30 years ago [1]. Nonaqueous polyelectrolyte solutions, aqueous Li^+-ion batteries, eutectic mixtures, superconcentrated or highly concentrated electrolyte (HCE) solutions have received much attention recently as strategies to overcome safety and environmental issues regarding conventional LIBs. In this work we employed molecular dynamics (MD) simulations to explore the solvation behaviour of sulfolane-$LiBF_4$ mixtures going to [$LiBF_4$] up to ca. 6 mol.L^{-1}. The MD results indicate that the relaxation dynamics of the contact ion pair and Li-sulfolane pair follows a Kohlrausch–Williams–Watts function. Under the assumptions of the Scher-Lax-Phillips (SLP) model [2], we demonstrate [3] that the relaxation behaviour of $LiBF_4$-sulfolane mixtures is analogous to that seen in glass-forming materials at much lower temperatures. At fully percolated conditions, i.e., in the presence of two continuous networks (cation-anion and cation-solvent), the relaxation of the contact ion pair is dictated by long-range Coulomb interactions, while density fluctuations play an important role in relaxation of the Li^+–sulfolane pair. Also, the largest contributor to the Stokes-Einstein breakdown in these mixtures is the cation-anion pair dynamics. The Li-ion transport changes from cage diffusion to hopping conduction, similar to the Grotthuss mechanism of proton transfer.

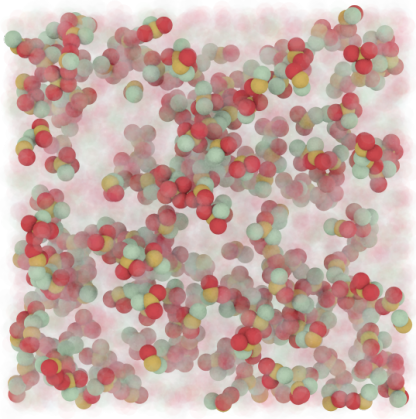

Figure 1. Simulation snapshot depicting the polar networks of the sulfolane/$LiBF_4$ mixture with molar fraction of sulfolane χ_{SL} = 0.68. The colours red, dark yellow and green represent O, Li and F atoms, respectively. Only the network nodes with Li^+ ions shared simultaneously by O atoms from sulfolane and F atoms from BF_4^- are highlighted in the picture.

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Valorization of the invasive macroalgae *Asparagopsis armata* through an integrative biorefinery approach

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Marine invasive species are widely recognized as a serious threat to marine ecosystem integrity, unbalancing native communities, which may lead to negative ecological and economic impacts. The red seaweed *Asparagopsis armata* is one of worst invaders in Europe and America and its exploitation to obtain natural bioactive ingredients represents a two-folded opportunity - high availability of biomass for the extraction of value-added compounds and/or new materials, and mitigation of the negative effects caused by alien species, contributing to ecosystem integrity and sustainability. Therefore, the aim of this study was to develop a green biorefinery process to sustainably explore this seaweed, obtaining antifouling extracts and using the final waste biomass to produce biochars. The antifouling properties were previously evaluated on micro and macrofouling species, with results suggesting a great antifouling potential [1,2]. The residual *A. armata* biomass was tested to produce biochars by pyrolysis (TC, conventional thermal carbonization in inert atmosphere) and by advanced processes, such as, hydrothermal carbonization (HTC) and acid-mediated carbonization (AMC) [3]. HTC allowed the most developed porous structure (BET area of 19 m^2/g and total pore volume of 0.05 cm^3/g) since TC and AMC yielded biochars with values one order of magnitude lower. Biochars have 22.9-34-7% of oxygen with the one prepared by TC presenting the higher number of heteroatoms (*e.g.*, Na, Si, S, Cl, Ca, and Al) due to its higher ash content (39% *vs* 8% for HTC and 10% for AMC). XRD of the *A. armata* ash points for the presence of $NaAlSi_3O_8$ (albite), NaCl (halite) and $CaCO_3$ (calcite and vaterite). Biochars surface chemistry characteristics depends on the carbonization process: TC yields a basic surface (pH_{PZC} = 8.1) while HTC and AMC originate an acidic surface (pH_{PZC} = 2.4 and 1.9, respectively). The morphology of the biochars (Fig. 1) reveals that AMC originates particles with a more compact structure.

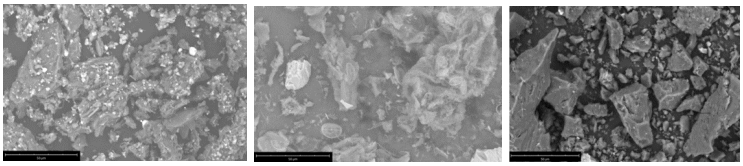

Figure 1. SEM images of the biochars obtained by TC (left), HTC (center), and AMC (right).

As this seaweed invader occurs in great amounts in Portugal and in many other coasts of the world, its collection and valorization could contribute for marine ecosystem restoration and integrity, promoting biodiversity and blue economy through a profitable harvesting to obtain ingredients with antifouling properties and new biochars with a broad range of industrial applications, turning a threat into major socio-economic opportunities.

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Can marine macroalgae dietary supplementation afford neuroprotection to waterborne inorganic mercury exposure in the fish *Diplodus sargus*?

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Marine macroalgae have a great potential since it is a source of many natural compounds essential with physiological benefits. Despite that, there is a poor knowledge on the impact of macroalgae supplementation to afford protection against environmental contaminants exposure in fish. Mercury is well recognized by its great toxicity, including the damage of the nervous system in fish (among other organisms). This study aimed to evaluate the neuroprotection afforded by a macroalgae-enriched diet to fish (*Diplodus sargus*) exposed to waterborne inorganic mercury (iHg) by covering the assessment of Hg toxicokinetics in the brain, together with effects related to oxidative stress and neurotransmission impairment. For this purpose, fish were fed during 3 months with a macroalgae-enriched feed [total incorporation of 5%, with the species *Ulva rigida*, *Fucus vesiculosus* and *Gracilaria gracilis*, equitably represented - algae supplementation (A)], while non-supplemented fish were fed with a standard diet (S). Then, both dietary background groups were exposed to waterborne iHg (2 µl L^{-1}) for 7 days (T7) (groups AHg and SHg), followed by a post-exposure period of 14 days (PE14). Control fish, unexposed to iHg, were maintained over the experiment (AC and SC). At T7 and PE14, fish of the different groups (AC, SC, AHg, SHg) were sacrificed and the brain was collected for the determination of total Hg levels, for the assessment of oxidative stress related parameters [superoxide dismutase (SOD), glutathione peroxidase (GPx), glutathione S-transferase (GST), glutathione reductase (GR), total glutathione (GSHt), and lipid peroxidation (LPO)] and acetylcholinesterase (AChE). Fish with a macroalgae dietary background accumulated significantly lower levels of Hg in the brain that those under a standard diet, both at T7 and PE14. Levels of Hg in the brain have not decreased in the post-exposure period in SHg and AHg fish, pointing out the slow elimination of iHg. Despite that, iHg exposure triggered poor signs of neurotoxicity, since no significant changes were recorded for antioxidants, lipid peroxidation and AChE. Only a slight increase of SOD in SHg fish was found at T7. Interestingly, fish under a macroalgae-enriched diet exhibited some changes of oxidative stress related endpoints upon exposure to iHg for 7 days, as a significant decrease of GPx, GR and GSHt. Also, AHg fish had lower AChE activities and showed an enhancement of LPO (tough not statistically significant) at T7. Macroalgae supplementation can afford protection against Hg accumulation in the fish brain, but an imbalance of antioxidants and neurotransmission related parameters may occur, pointing out the need of further studies to disclose the neuroprotection mechanisms.

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Solvent Extraction of Palladium by a New Thiodipropanamide Derivative

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Platinum group metals (PGMs) exhibit unique properties that justify their extensive technological application. Accordingly, their high economic value, difficult replacement and rarity have determined the classification of PGMs by the European Union as critical raw materials. The catalytic activity of PGMs is the most exploited property, and it is in this function that their main uses are focused, with emphasis on automotive catalysts (essential for minimizing the emission of toxic exhaust gases from combustion engines), and industrial catalysts (for example, in petroleum refining and in the petrochemical and pharmaceutical industries) [1].

In sequence of previous research, aiming to contribute to the development of hydrometallurgical operations allowing a good recovery of PGMs, namely platinum and palladium, from automotive or industrial catalysts, a preliminary evaluation of the solvent extraction performance towards Pd by a new organic extractant, *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodipropanamide (DMDCHTDPA), similar to another already tested, *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) [2,3], is described.

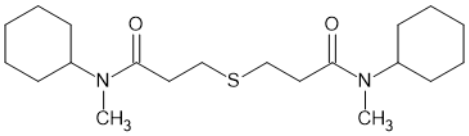

Figure 1. Structure of DMDCHTDPA.

DMDCHTDPA was synthesized and properly characterized. The carried-out tests showed DMDCHTDPA in toluene to be a very efficient solvent to recover Pd from dilute and concentrated HCl solutions, from which the PGM can be stripped by an acidic thiourea aqueous phase. Equilibrium distribution data allowed proposals for the most probable Pd extraction reactions involved. DMDCHTDPA shows a good Pd loading profile and a promising behavior for a proper reutilization in successive extraction-stripping cycles. Preliminary results obtained on the use of the DMDCHTDPA solvent to selectively recover Pd from model and real leaching solutions of spent catalysts are presented and adequately discussed, and compared with data achieved with other commercial extractants as well [4].

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Perfluorinated (PFAS) Pollutants in Water – Interfacial Properties and Diffusion Coefficients for Environmental Remediation Processes

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The environmental contamination with synthetic per- and polyfluoroalkyl substances (PFAS, defined by OECD as fluorinated substances with at least one fully fluorinated methyl or methylene carbon atom) has gained exponential attention in the last two decades, following the discovery of their bioaccumulation potential and of connections to severe human health issues. States are issuing ever more restrictive legislation on PFAS production and use, and tightening the limits on their presence in food, drinking water and effluents. PFAS are now ubiquitous in the environment and, due to their extreme chemical inertness, simply phasing-out the production and application of these substances is not a reasonable strategy to deal with the problem. The number of PFAS remediation plants is thus increasing rapidly in several parts of the world and is expected to continue accelerating in the near future.

The foam fractionation process has very recently emerged as a successful treatment for PFAS contaminated waters. It relies on the surfactant properties of most of the pollutant PFAS, separating them by adsorption to gas bubbles rising through a column of water, which form a layer of foam that is extracted. This method does not produce solid wastes, is energy efficient, and has already been successfully used at full scale to achieve the remediation of different water streams ranging several orders of magnitude of PFAS concentrations. Hence, it has the potential to become the dominant technology, a sustainable alternative to the more usual adsorption or membrane methods.

The development, optimization and modelling of this novel technology crucially depends on the detailed knowledge of the behaviour of these peculiar surfactants in water, in particular of their diffusion coefficients and of the adsorption properties at the liquid/vapour interface. In this work, the diffusion and interfacial behaviours of target regulated PFAS in water are studied by molecular dynamics simulations (MD), focusing on the effect of the ionic strength of the water matrix and on the structure of the perfluorinated surfactant. The molecular models and simulation methods are validated against the available literature results, and then used to obtain properties for related compounds, to extrapolate beyond the experimentally studied conditions, and to obtain a molecular-level understanding of the observed phenomena.

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Green Extraction Process of Phenolic Compounds from Portuguese Macroalgae

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Seaweeds are naturally abundant, do not require crop fields and have a low requirement in terms of land. Also, they do not present competition for food, while producing several biologically active secondary metabolites of great interest [1,2]. In this work, Sargassum muticum is a brown seaweed was used as a source of biomass. Given its invasion and difficulty of removal through harvesting, it can be considered a biowaste [3]. It is well known that seaweed presents a significant amount of phenolic compounds (PCs), and species belonging to Sargassaceae family are recognized to have a particular high quantity.

The aim of this study was to evaluate the performance of eutectic solvents (ESs) in the extraction of PCs (gallic acid, 3,4 dihydroxybenzoic acid, caffeic acid, syringic acid, p-coumaric acid, ferulic acid, salicylic acid, catechin and quercetin) from Sargassum muticum. Several betaine-based, proline-based, and choline based ESs were tested for the extraction of PCs. Proline combined with propylene glycol (Pro:PPG) exhibited the higher yield according to HPLC results, followed by proline:1,2-butanediol (Pro:1,2-But) and choline:citric acid (ChCl:CA). Pro:PPG also presented high selectivity towards salicylic acid, meanwhile ChCl:CA towards gallic acid. Optimizations studies of water content and temperature were performed for the three best ESs, being the optimum conditions at 30% (v/v) of water and 60°C of extraction temperature. Ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE) were two intensification methods evaluated to enhance the extraction process, proving their ability to reduce the extraction time when compared with the conventional solid-liquid extraction (SLE) process. In particular, Pro:PPG-based MAE provided a significantly higher extraction yield in comparison with conventional extraction and with the other extraction solvents.

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Liquid-liquid equilibria of asymmetric ionic liquids and water

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Due to their tunability, ionic liquids (ILs) are among the most distinctive chemical families. The unique characteristics of ILs, also known as designer or task-specific solvents, are due to the wide variety of cations and anions that can be combined [1]. In the chemistry of ILs, the bis(trifluoromethylsulfonyl)imide ([NTf_2]-) anion is one of the most iconic and widely used and it is symmetric in nature [2]. This study focused on "altering" a part of the [NTf_2]- anion, either by lengthening the fluorinated chain or introducing different moieties like (-COOH, -$C(CN)_2$) and (-N(CN)), making it assymetric. Another studied asymmetric anion was [F_3CBF_3]-, which is compared to [BF4]- anion (Fig.1). all these anions were studied in ILs with [C_2mim]+ cation (Fig.1). The insertion of asymmetry in anions has a significant effect in the reduction of viscosity and melting point [3].

In this work, we advance our understanding of the liquid-liquid phase equilibria of binary mixtures of IL+water.

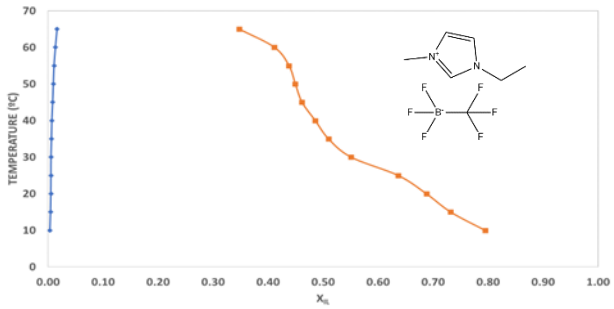

Figure 1. Liquid-Liquid phase equilibria diagram for water and IL ([C_2mim][F_3CBF_3]) as a function of ILs mole fraction. The lines are just to guide the eye.

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New insights into interactions between marine biota and Platinum Group Elements

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Understanding the impact of Platinum Group Elements (PGEs) in the environment requires suitable analytical techniques and an array of environmental samples that are usually complex matrices. This work addresses the occurrence of PGEs in seawater and the contamination levels in several species of macroalgae (brown algae *Fucus sp.*, red algae *Mastocarpus stellatus* and *Chondrus crispus*, as well as green algae *Ulva sp*) and mussels (*Mytilus galloprovincialis*). Samples were collected in two estuarine systems and adjacent coastal areas (Douro and Ave estuaries, North of Portugal) during two contrasting seasons [1]. Dissolved concentrations (PGE_{diss}; <0.2 µm) measured by adsorptive cathodic stripping voltammetry (Ad-CSV) were higher in the Ave Estuary than in the Douro Estuary for both trace elements. The PGE_{diss} varied between the detection limits (DL ~0.01 $ng{\cdot}L^{-1}$) up to 1.98 $ng{\cdot}L^{-1}$ for Pt and 0.04 $ng{\cdot}L^{-1}$ for Rh. In wastewaters from a treatment plant in the Ave watershed, dissolved Pt reached 8.61 $ng{\cdot}L^{-1}$, whereas dissolved Rh was below DL. As to Pt and Rh in biota, measured by inductively coupled plasma mass spectrometry (ICP-MS), concentrations found in macroalgae from the Douro Estuary varied from 0.18 to 0.55 $ng{\cdot}g^{-1}$ and from ~0.05 to 0.78 $ng{\cdot}g^{-1}$ for Pt and Rh, respectively. These were similar to those found in the Ave Estuary. Concentrations of Pt and Rh found in mussels varied between 0.01 $ng{\cdot}g^{-1}$ up to 0.22 $ng{\cdot}g^{-1}$ for Rh and >1.0 $ng{\cdot}g^{-1}$ for Pt, with the highest values generally measured in winter season.

No significant seasonal differences were recorded, highlighting the constant pressure exerted in urbanized estuarine systems. Variations in the concentrations and Pt/Rh ratios in those organisms might be explained by bioaccumulation/sorption pathways that may occur differently for macroalgae and mussels (e.g. passive sorption vs active filtration). Yet, the coupled use of dissimilar bioindicators could provide a more integrative study of PGE contamination levels in estuarine/coastal environments, complementing a sampling strategy for monitoring purposes. As macroalgae and mussels represent two food resources for higher aquatic organisms and directly or indirectly for human consumption, careful study of potential ecotoxicological implications of PGE contamination in aquatic media is required.

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Bar Adsorptive Microextraction – A novel strategy in doping control for the qualitative determination of Alkyl Amines Stimulants in urine matrices

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During the development and implementation of analytical methodologies in anti-doping control, the main goal consist in obtain undoubtedly and irrefutable technical and scientific results, in compliance with the World Anti-Doping Agency (WADA) requirements. The introduction of modern sample preparation techniques is extremely important, mainly when using complex biological matrices. Simultaneously, added value comes up with boosting analytical enrichment together with strong reduction or elimination of interferents and, thereby, achieving correct identification and quantification of the target analytes. In the last decade, bar adsorptive microextraction (BAμE) has emerged as a new perspective in sample preparation following the green chemistry guidelines. This device has proven to be a robust analytical approach in several applications, in order to overcome the limitations presented by other technologies, such as stir bar sorption extraction or solid phase microextraction. [1-5]

The present contribution proposes a new analytical approach for the qualitative determination of six alkyl amine (AA), namely 1,3-dimethylbutylamine, 1,4-dimethylpentylamine, heptaminol, isometheptene, octodrine and tuaminoheptane using BAμE followed by gas chromatography coupled to mass spectrometry operating in the selected ion monitoring mode acquisition (GC-MS(SIM)). After selecting the best sorbent material and achieving the best microextraction conditions using 1 mL of urine sample, a complete validation procedure was performed. The proposed methodology showed excellent selectivity/specificity, suitable limits of identification (LOI, 5.0-35.0 ng/mL), appropriate linear dynamic ranges (5.0-200.0 ng/mL) with good determination coefficients (r^2 > 0.9937), as well as good robustness, accuracy and repeatability in intraday and interday conditions at two different levels. To check whether the methodology is fit-for-purpose, four previously analysed proficiency urine samples were successfully tested, in which were unequivocally detected and identified some of the target AAs in compliance with WADA guidelines.

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Manufacturing chitosan and alginate films and 3D structures with potential antioxidant activity

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The research and development of three-dimensional (3D) printing for biomedical applications has increased significantly during the last decade [1]. The development of natural biomaterials with enhanced biological properties, due to their biocompatibility, is currently an expanding area with a considerable potential to explore. Antioxidants have been proposed to control oxidative stress in wounds and accelerate their healing process [2]. The combination of biopolymers with proved antioxidants compounds can give added value to the final composite material for production of wound dressing films or other healthcare applications. In this context the present study reports the production of chitosan and alginate films doped with ascorbic acid and quercetin, both compounds with proved antioxidant activity. Films of the hybrid blends were produced by casting method and chemical and mechanical characteristics were determined. Antioxidant activities were determined by ABTS and DPPH standard methods and results showed, that in general, the composites retain the main antioxidant activity of the compounds. Three-dimensional structures were produced by syringe extrusion and the prototype were optimized.

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Effect of the synthesis conditions on the photocatalytic activity of pure and sulphur modified BiOCl

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Over the past few decades, as industry has progressed, so too has our concern on the effect of its products in the environment. As a result, the need for decontaminating wastewater has motivated the development of pollutant removal methodologies, such as the use of nanoparticles for adsorption and photocatalytic degradation [1,2].

In the present work, nanoparticles (NPs) of bismuth oxychloride (BiOCl) were synthesized by two methods, hydrolysis (BiOCl-h) and solvothermal (BiOCl-t), and those were characterized by XRD, DRS, SEM and TEM. The results suggest the formation of sheet-like crystalline BiOCl-t NPs with very small size (width 20-100 nm and thickness 15-20 nm), organized in spherical agglomerates of approximately 3-10 μm, Figure 1. Whereas for BiOCl-h dispersed, slightly bigger and thinner sheets were formed (up to 400 nm and 5-15 nm thick). Both samples display similar optical properties (bandgap energy, E_g ≈ 3.5 eV). A higher surface area was obtained for the BiOCl-h NPs (23.234 $m^2 g^{-1}$) as compared with the BiOCl-t sample (12.207 $m^2 g^{-1}$).

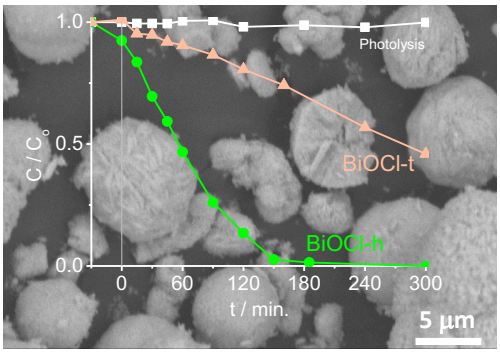

Figure 1. SEM image of BiOCl-t aggregates and photocatalytic response of the prepared samples towards caffeine (10 ppm) degradation.

These nanoparticles were modified with sulphur using different precursors. Although their characterization, by the same techniques, showed no influence on the BiOCl-S NPs size and aggregation, and a decrease of crystallinity and of E_g to 3.40, 3.00 and 3.40 eV, for precursors 1 to 3, respectively, was obtained.

The photocatalytic activity of the prepared NPs was assessed under visible radiation for the degradation of caffeine. The analysis by UV-Vis spectrophotometry allowed to conclude that all these photocatalysts promote the photodegradation of the pollutant under study, as compared to photolysis, Figure 1. So far, the best response was obtained by BiOCl-h, degrading all the caffeine present in the solution in approximately 150 minutes.

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Molecular Dynamics Simulations of Hydraulic Binders with low CaO/SiO_2 ratios

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Worldwide production of cement generates 5 to 8% of all anthropogenic CO_2 emissions. Most of the emissions of cement production result from the decarbonation of limestone, $CaCO_3$, to yield quicklime, CaO, through the reaction $CaCO_3 \rightarrow CaO + CO_2$. Quicklime and silica, SiO_2, are the two main components used in the production of cement precursors, also known as clinkers, but generally other metal oxides may be present such as Al_2O_3 and Fe_2O_3.[1]

Recently, we have been investigating the possibility of formulating new cement clinkers with lower quicklime to silica (C/S) ratios, thus reducing the amount of CO_2 released to the atmosphere during the process.

This work is focused on the characterization of these novel hydraulic binders at the atomic/molecular level with the help of Molecular Dynamics simulations, including the study of their structure and elemental composition, the nature of their crystalline/amorphous phases, the elucidation of the different reaction mechanisms (hydration and carbonation reactions) and the estimation of their mechanical properties.

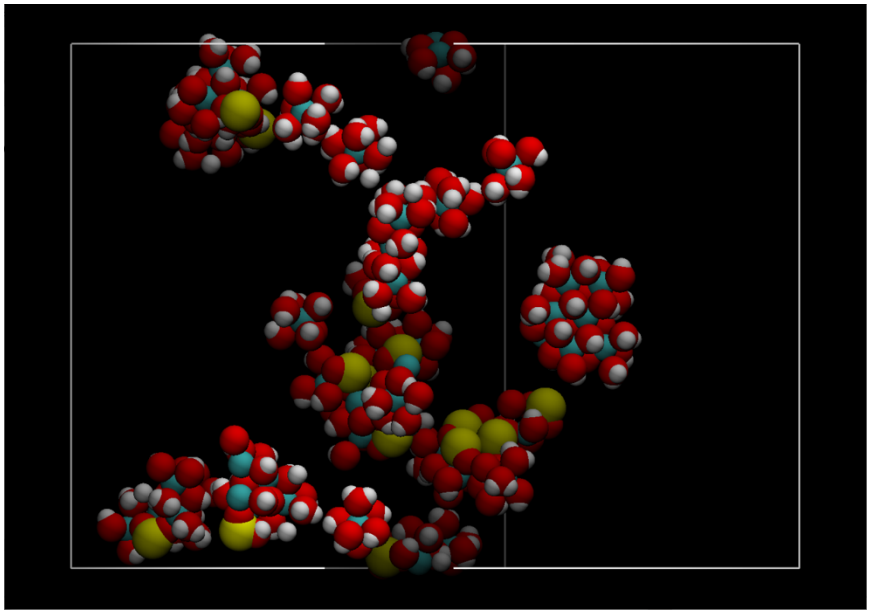

Figure 1. Snapshot of a solution of H_4SiO_4 and $Ca(OH)_2$. This picture shows the beginning of the formation of a nanocrystal of $Ca(OH)_2$, a known product of cement hydration (●-Ca; ●-Si; ●-O; O-H).

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A new approach to enhance the characteristics of sustainable integrally skinned monophasic hybrid cellulose acetate/silica membranes for ultrafiltration

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The present work proposes a novel approach to optimize the ultrafiltration performance of sustainable integrally skinned monophasic hybrid cellulose acetate/silica membranes.

Two membranes series (1 and 2) with different formamide/acetone ratio (0.57 wt.% in series 1 and 0.73 wt.% in series 2) and increasing the amount of silica (from 0 wt.% up to 30 wt.%, with increments of 10 wt.%) in each series were studied.

The membranes' morphology was analyzed by scanning electron microscopy (SEM), and the chemical composition by Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR). The hydraulic permeability of the membranes was evaluated by measuring pure water fluxes following membrane compaction. A higher formamide/acetone solvent ratio led to thicker membranes (series 2) with higher hydraulic permeability values (47.2 – 26.39 kg.h-1.m-2.bar-1) than for the membranes in series 1 (40.01 – 19.4 kg.h-1.m-2.bar-1).

The two TEOS-formamide and cellulose-acetate-formamide spinodal decompositions occur sequentially originating an accurate monophasic system. The non-hydrolysable organic groups (-NH2 and (CH2OCH)CH2O(CH2)3) will stay in the final hybrid membrane and will be suitable for adsorbing nitrogen-based products in liquid aqueous media.

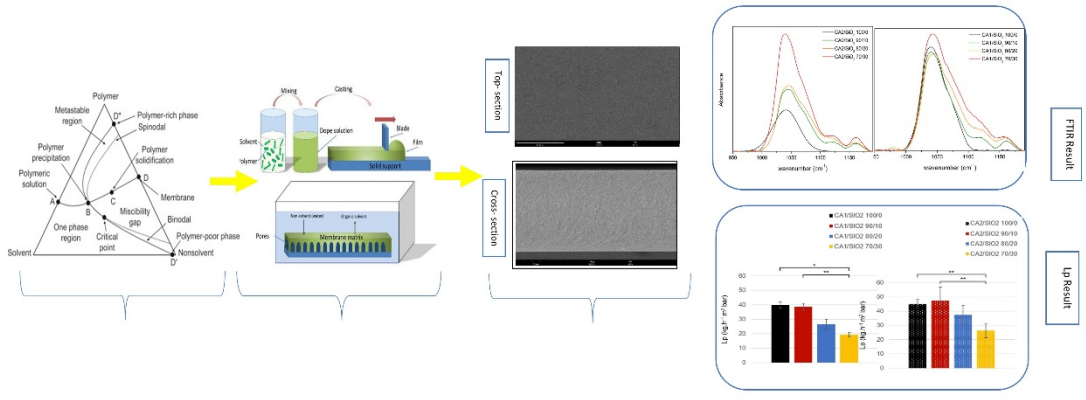

Figure 1. Graphic Abstract

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/20; Ciência e a Tecnologia (FCT, Portugal) through the CeFEMA programmatic funding UIDB/04540/2020 and UIDP/04540/2020. IDMEC researchers acknowledge Fundação para a Ciência e a Tecnologia (FCT, Portugal) for its support through project IDMEC under LAETA, project UIDB/50022/2020.

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P75

Membrane preparation from the Black Soldier Fly exuviae

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With the increase in world population, it is extremely necessary to preserve the water resources of the planet. Thus, the objective of this work, carried out within the scope of the chemical engineering master's thesis “Valorization of industrial biomass for water treatment”, is to develop a prototype, in this case a membrane, able to remove pollutants and hazardous metals from wastewater. For the membrane substrate, chitosan biopolymer is used. This chitosan is obtained by the deacetylation of the chitin present in the black soldier fly exuviae. The first challenge of this project was therefore the quantification of the amount of chitin in each exuviae with different methods. The second challenge was chitin quantification on starting material and its transformation into chitosan based in different methods. The preparation of chitosan membranes based on existing protocols will be discussed.

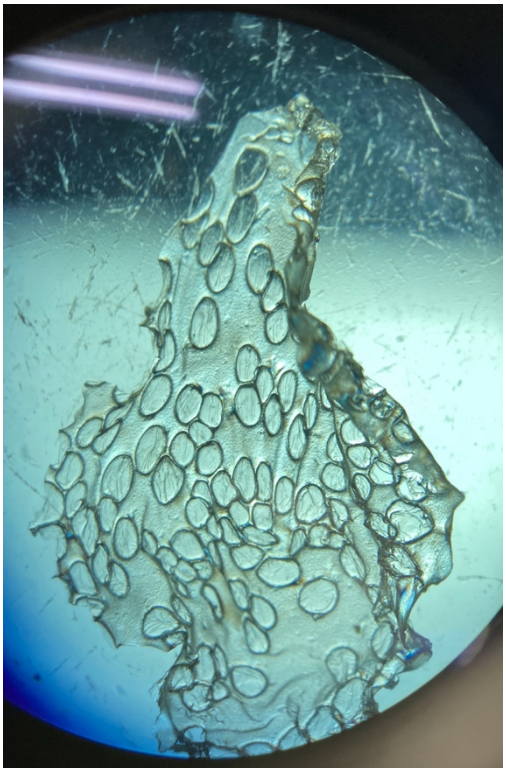

Figure 1. Chitosan Membrane

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

P76

Valorization of abundant Portuguese biomass by carbonization and activation processes

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Sustainable development and the implementation of a circular economy require a rational and efficient use of natural resources. Biomass is a renewable resource and can partly replace fossil fuels and thus reduce CO_2 emissions. In fact, biomass can be utilized for energy production or converted into other types of fuels or materials, as is the case of biochar, which can serve as an energy source, adsorbent, soil additive or precursor for the synthesis of activated carbons. Valorizing abundant plant resources to produce value-added materials, such as biochars and activated carbons, is a central research topic [1]. Biochars present a great potential to improve soil properties and plant growth [2], and activated carbons play a key role in improving wastewater treatment processes aiming at higher removal of contaminants of emerging concern that are a threat to ecosystems and human health [3].

In this work three abundant and different types of biomass collected in Portugal were explored: *Acacia longifolia* and *Carpobrotus edulis* (both invasive species) and *Cistus ladanifer* (native species). After being collected in the field (*Acacia* and *Carpobrotus* in Vila Nova de Mil Fontes (Alentejo) and Cistus in Barão de São João (Algarve)) all were dried to constant weight and cut to uniform pieces (< 5 mm). Two carbonization processes were tested: pyrolysis at 400 ºC during 1h under N_2 flow of 5 cm^3/s and hydrothermal carbonization (HTC) at 170 ºC during 24h. Pyrolysis of *Carpobrotus* attains a yield of ~ 50% while for *Acacia* trunk it is only ~29%. For the HTC of *Carpobrotus* the yield is ~ 40% while for *Acacia trunk* is ~ 53%.

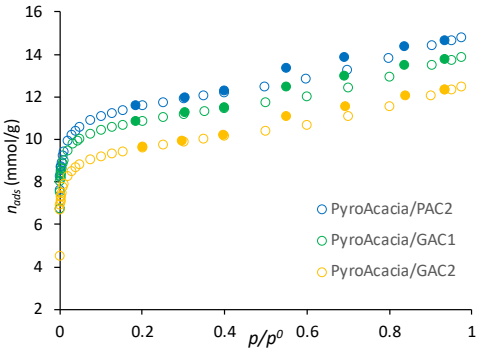

Figure 1. N_2 adsorption isotherms of PyroAcacia-derived activated carbons.

Steam activation of *Acacia* trunk pyrochars allowed to obtain both powdered and granular activated carbons (PACs and GACs, respectively) with micro-mesopore networks and BET area values close to 1000 m^2/g. Studies on the activation of biochars obtained from HTC and from *Carpobrotus* and *Cistus* obtained from pyrolysis and HTC are ongoing. In another perspective, selected pyrochars and hydrochars will be assayed as a soil amendment since these carbon-rich materials might improve soil moisture retention and favor higher growth and survival rate of plants [3]

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. ASM thanks FCT for the Assistant Researcher contract CEECIND/01371/2017 (EMBRACE Project).

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P77

Recovery of metals using deep eutectic solvents

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The recovery of metals from wastes is a great challenge of our time since the demand for these materials is continuously growing. This is essentially due to the energetic transition towards cleaner and more environmentally friendly technologies that is moving towards the implementation of more renewable energy sources and electrification, processes that will require a great amount of metals and that will produce also many metallic wastes. Moreover, sources are not unlimited and the continuous request and exploiting can lead to some of these materials to be endangered for future supplies. In future, there could be a point at which the supply of these materials will not compensate the demand and their usage will be consequently limited, or their economy will not be favoured anymore.[1] Some institutions tried to resume which will be the future elements at supply risk (American Chemical Society, Figure 1), others made a list to establish which are the critical raw materials (CRMs) nowadays and in the next years (EU [2], USA), based on relative abundance, economic importance in strategic sectors and geopolitics of those elements. The recovery of these elements is very important, and in a context of sustainability and circular economy, looking for greener alternatives to the present recovery methods deep eutectic solvents (DES) gained many attentions and new more sustainable recycle pathways are being developed with these new classes of solvents. The aim of the project is the recovery of metals experiencing the use of DESs, analysing all the recovery processes and looking for the highest selectivity and the most sustainable ones in order to make the recovered material available for new purposes.

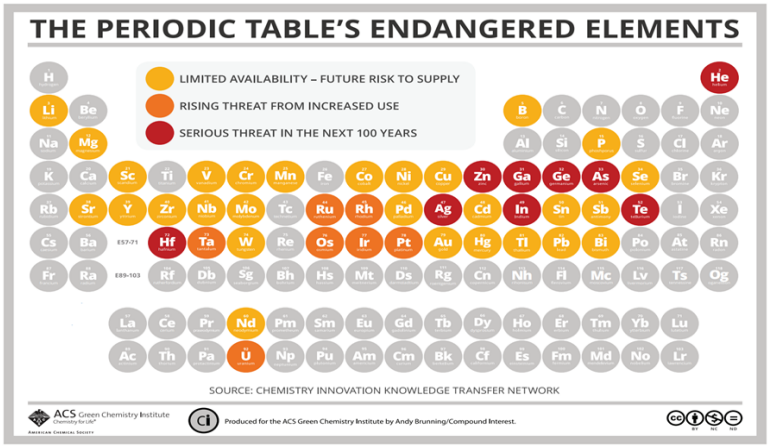

Figure 1. American Chemical Society periodic table of endangered elements. [3]

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P78

Valorization of lignin-based electropolymerized films as platforms for immunosensors

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The current global environmental challenges imply the reduction of harmful chemicals and the valorization of beneficial compounds that are abundant in agro-industry wastes. There are about 50 million tons of lignin produced every year as a sub-product of paper industry, and is still considered has an industrial low-value product, being essentially used as fuel [1]. The lignin polymer is mainly composed by three structural monolignol units: syringyl, guaiacol and p-hydroxyphenyl moieties that are connected in a three-dimensional network through multiple linkages [2]. The presence of aromatic groups and the possibility for chemical derivatization provides attractive physicochemical properties to lignin-based products, namely, energy storage and adhesiveness.

This work aims to explore highly adhesive and biocompatible polymeric interfaces, suitable for biosensing, through the valorization of low-weight unpurified lignin fractions. To this end, lignin derivatives were electropolymerized to produce a thin polymer, enriched with catechol moieties, resembling polycatechol coatings [3]. Several parameters were tested to determine the optimal conditions for the electrosynthesis, namely electrochemical mode of polymerization, solution pH, supporting electrolyte, and the optimal concentration of the lignin fraction. The resulting polymers were analyzed in terms of electrochemical behavior, catechol surface coverage, wettability, deposited mass, and ability to transduce the redox conversion of soluble species. The thickness and morphology of the polymer films were determined using ellipsometry and atomic force microscopy (AFM), whereas electrochemical quartz crystal microbalance was used to assess the deposited polymeric material. Preliminary Surface Plasma Resonance (SPR) assays showed very promising results concerning robust protein adsorption onto lignin-based polymeric matrix, without requiring any previous chemical activation step. In particular, the electrogenerated polymers were successfully tested for the specific affinity interaction between Immunoglobulin G and its antibody. This is a simple and versatile platform that can be adapted for any target antibody/antigen couple.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. The funding from the Bio Based Industries join Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No. 792061 (SWEETWOODS) is acknowledged.

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P79

Solubility of CO_2 in Ionic Liquids by Molecular Dynamics

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Human activities, such as burning fossil fuels and deforestation, have caused an increase in greenhouse gas concentration in the atmosphere, resulting in noticeable climate change and its associated impacts. Carbon dioxide (CO_2) is one of the primary greenhouse gases and plays a crucial role in regulating Earth's temperature and climate by regulating the carbon balance between the atmosphere, land, and oceans [1]. To mitigate these effects, it is essential to manage and reduce CO_2 emissions. Ionic liquids (ILs) have emerged as a promising solution due to their wide range of properties, including excellent solvation capabilities. Their ability to solvate polar solutes with large dipole and quadrupole moments, such as CO_2, makes them an attractive option [2]. However, the solubility of gases in ILs is greatly influenced by the nature of the IL anion, which can be adjusted with the appropriate combination of ions. Moreover, Molecular Dynamics (MD) simulations have proven successful in studying IL properties at a molecular level. Therefore, this work aims to conduct a systematic MD study of CO_2 in different types of imidazolium-based ILs to gain a better understanding of their structural behavior and how it can be tuned for capture and storage of green-house gases.

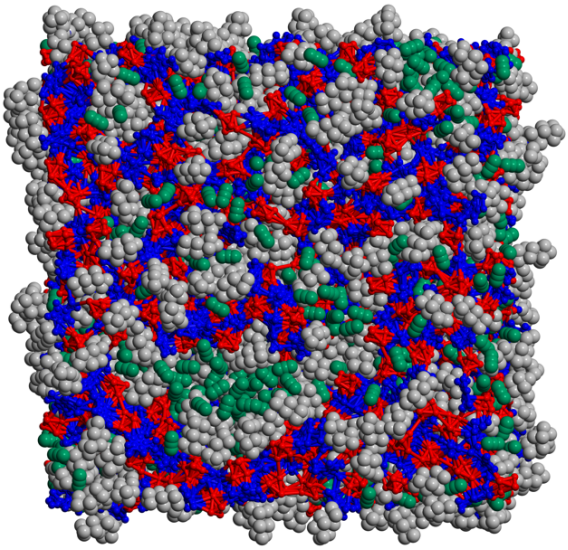

Figure 1. Snapshot of the MD simulation box performed for an equimolar mixture of $[C_6C_1im][TFO]$ and CO_2. The blue and red colors depict the polar part of the cations (imidazolium ring) and anions (triflate), respectively, the grey color represents the nonpolar alkyl chain of the ionic liquid and the green color corresponds to the carbon dioxide molecules.

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P80

Headspace-bar adsorptive microextraction for evaluation of biogenic volatile organic compounds

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Currently, one of the major environmental concerns is the frequent occurrence of forest fires, particularly under extreme atmospheric conditions. Some studies suggest that higher temperatures lead to a greater emission of biogenic volatile organic compounds (BVOCs), produced, and accumulated in different plants, becoming extremely flammable gases in the event of forest fires. Consequently, in the presence of an ignition source, BVOCs can contribute to the spread of forest fires, leading to catastrophic events, as was the case with the 'Pedrogão Grande' tragedy (Portugal) in 2017 [1,2]. Thus, it becomes relevant to study the composition of BVOCs even more in depth, especially the terpenoid fraction, consisting of compounds such as α- and β-pinene, limonene, 1,8-cineole, and thymol, since they are among the most abundant monoterpenes in trees and shrubs, and even some oxygenated sesquiterpenes, such as caryophyllene oxide [3]. Therefore, it is important to develop and apply effective methodologies that allow the identification of the main BVOCs present in trees and shrubs, highlighting the use of analytical tools such as bar adsorptive microextraction in the headspace mode, an easy-to-use and eco technique combined with gas chromatography-mass spectrometry (HS-BAμE/GC-MS) [4].

The present work aims to apply, optimize, and validate the HS-BAμE/GC-MS methodology to monitor the main BVOCs emitted from several common shrubs in Portugal, namely *Cistus Ladanifer* and *Cistus Monspeliensis*, *Erica Scorparia*, *Lavandula Stoechas* and *Thymus Villosus*. The performance, advantages and limitations of this novel approach is also addressed [5,6].

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P81

Treated wastewater used in germination and growth of onions and carrots

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The agricultural sector is responsible for the consumption of 75 % of the total water used in Portugal [1]. With the increase in water demand worldwide and the scarcity in some regions, there is a need to find different mechanisms to guarantee that demand, namely in the agricultural sector. One of the solutions for reducing the consumption of freshwater in agriculture is the use of treated wastewaters (TWW) in irrigation. The reuse of TWW contributes to the reduction of the environmental impact by reducing the discharge of water into the environment and to the circular water system. Another advantage of the reuse of TWW is their rich composition in essential nutrients for crop growth, decreasing the need for fertilization. However, the TWW do not only contain beneficial nutrients for plants. Due to industrial wastewater, TWW can be contaminated with heavy metals that can be harmful for both crop development and public health. In Decreto-Lei nr. 236/98 of 1 of August [2], emission limit values (ELV) for several parameters namely, for toxic metals such as cadmium (Cd), lead (Pb), chromium (Cr) and nickel (Ni) are defined for wastewater discharges. To be used in irrigation TWW must comply with those ELV.

In this work, the impact of the use of TWW and TWW supplemented with Cd, Pb, Cr and Ni in ELV's concentration for watering onions and carrots during germination and growth was studied. The results show that the irrigation with TWW or TWW supplemented does not significantly influence the germination rate of the studied seeds or the growth of seedlings in the early days after germination. Considering tap water as a reference, carrot seeds showed an increase of 4 % in the germination rate when irrigated with TWW supplemented with metals, but no difference in this rate for irrigation with TWW. On the other hand, onions showed a 7 % decrease in the germination rate when irrigated with TWW supplemented and do not show any changes in this rate when irrigated with TWW and compared to those irrigated with tap water.

Studies on the effect on the growth and development of onions and carrots irrigated with these waters are under development, as well as the impact that TWW can have on the macronutrients available in each cultivated species.

This study about germination shows that species can be irrigated with TWW during their germination phase without observed harmful effects on germination rates. For TWW supplemented with metals, there is an increase of the germination rate for carrots and a decrease for onions.

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P82

Extraction of lanthanides studies from low metal concentration wastewater

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Lanthanides are critical elements and their recovery from wastewaters increase availability of these elements and reduce their impacts in the environment. In this study tentative approaches to extract lanthanides from low concentration aqueous solutions were investigated. PVDF membranes soaked with active compounds or synthesizing chitosan-based membranes that contains those active compounds were used. The use of chitosan for this purpose is a novelty. The capability of those membranes was accessed by simulated extractions in 10^{-4} M aqueous solutions of lanthanides measured by ICP-MS. Some membranes could achieve a maximum concentration factor for the final solution relative to the initial one higher than 13 times for Yb, obtained with a chitosan-sucrose-citric acid membrane. Several of those chitosan membranes can extract around 10 mg of lanthanides per gram of membrane, being the better one the membrane with sucrose/citric acid that achieve more than 18 mg/g of membrane (Figure 1). These membranes are easily prepared and at very low cost and practical applications can be envisaged in near future.

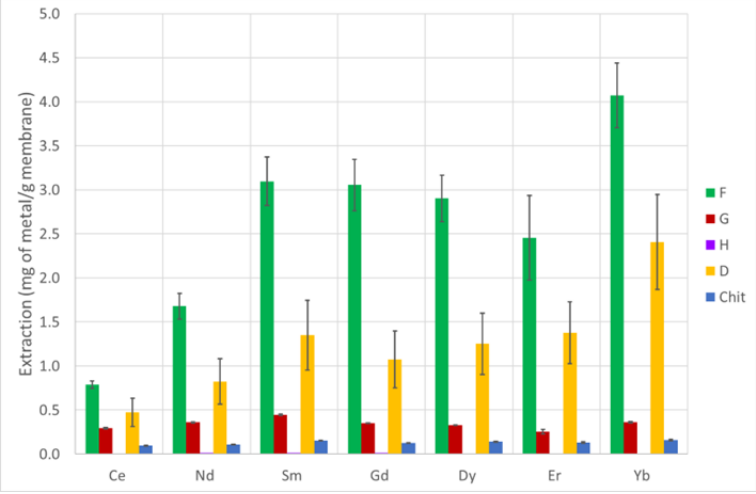

Figure 1. – Extraction of each metal studied by chitosan-based membranes with several active compounds irradiated at 5 kGy with a dose rate (DR) of 0.5 kGyh^{-1}.

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Extraction of Phenolic Compounds from *Ananas comosus* Processing Biowaste for Cosmetic Applications

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Ananas comosus, commonly recognized as pineapple, is a tropical fruit consumed fresh or processed as juice, canned fruit, jam, or concentrates. Pineapple processing residues (peels, core, stem, and crown) are not consumed, accounting for nearly 50% of the total pineapple weight [1]. Pineapple processing industries generate considerable amounts of waste, representing a financial challenge, and an environmental threat. Nowadays, these residues are either disposed for composting, animal feedstock or burned. Many studies focus on the valorization of these bio-residues for a myriad of purposes, such as development of vegan leather [2], vinegar production [3], edible bio composites [4], nevertheless, few explore their application in cosmetics.

Pineapple biowaste is rich in phenolic compounds (ferulic acid, gallic acid, catechin, epicatechin, chlorogenic acid, caffeic acid, and cinnamic acid, among others) that can provide antioxidant and anti-inflammatory properties in topical formulations. Typically, the extraction of phenolic compounds from plant matrices is performed using conventional organic solvents (p.ex. ethanol, methanol, acetone), high temperatures, and/or pressures which can be time and energy consuming, require large amounts of solvents, and may produce toxic waste products. Yet, consumers' awareness to obtain these compounds through a more sustainable and greener processes, and the demand for cosmetic purposes creates a need to develop novel extraction techniques.

This study assesses the extraction of phenolic compounds using eutectic solvents (ES) that are readily applicable in cosmetic formulations. Since the phenolic compounds vary depending on the variety of the pineapple, two different varieties (cayenne from Azores, and MD-2 from Costa Rica) were chosen. Betaine and L-proline based ESs combined with sucrose, glucose, xylitol, urea, and glycerol were evaluated as extraction solvents. The extracts were analyzed through colorimetric methods where the total phenolic content, total flavonoid content, and antioxidant activity of the pineapple residues was quantified. Ratio and water content optimization were also performed after for the ES that showed better results through the colorimetric methods in the screening.

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Natural Eutectic Solvents based on Flavonoids and Terpenes

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Deep Eutectic Solvents (DES) are homogenous mixtures that enable a deep depression of the melting point of their parent compounds [1]. Contrary to simple Eutectic Solvents (ES), that have been long used in pharmaceutical field, only recently DES started to be considered as promising candidates for different applications in the pharmaceutical field, from solvents in the synthesis and preparation of compounds or through the formulation of bioactive compounds with another compound in order to obtain liquid formulations, often with synergy of properties [2]. This interest stems from the wide properties tunnability of these solvents, which is given not only by the chemistry of the constituent compounds but also by the possibility of changing the mixture composition.

An important class of biologically active DES or ES are the so-called Natural Deep Eutectic Solvents (NADES), that use only natural compounds, at least one with biological activity [3]. In this work, (D)ES will be prepared using bioactive natural compounds, namely flavonoids and terpenes, so that liquid mixtures at room temperature or body temperature can be obtained. These (D)ES will be characterized in terms of their solid-liquid phase diagram, so that the liquid window can be evaluated, thermophysical properties, including water solubility, density, viscosity, and also their biological properties, through cytotoxicity essays.

Figure 1. Natural Deep Eutectic Solvents.

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Sulfur-based ionic liquids as additives to lubricate bearing steel under extreme pressure conditions

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Steel is widely used in bearings of vehicle parts, turbines, engines and varied manufacturing equipment as it is a hard and very resistant material. Steel-on-steel contact caused by lack of efficient lubrication leads to energy losses and increased energy consumption, which represents an issue for several industries.

Ionic Liquids (ILs) are low-melting organic salts with very interesting properties as neat lubricants or lubricant additives. They exhibit high chemical and thermal stability, almost negligible vapor pressure, high ionic conductivity, non-flammability and ease in dissolving organic, inorganic and polymeric materials. One of the most attractive characteristics of ILs is related with the possibility to design the cation-anion combinations according to the desired properties as well as the final application. By choosing the adequate cation/anion combination, low viscosity fluids with adequate lubricant performance for specific metallic contacts can be obtained.

In this work, three ILs based on sulfur-containing anions – 1-hexyl-methylimidazolium trifluoromethanesulfonate ([C_6mim][TfO]), 1-hexyl-4-picolinium trifluoromethanesulfonate ([C_6-4-pic][TfO]) and 4-picolinium hydrogen sulfate ([4-picH][HSO_4]) – were tested and the first two stood out as promising additives. These ILs were studied as 2 wt.% additives to base oil polyethylene glycol MW 200 (PEG 200) to lubricate ASTM 52,100 bearing steel contacts under extreme pressure conditions (1.12 GPa) using a Mini-Traction Machine (MTM). MTM tests were conducted under mixed rolling-sliding conditions, which mimic several real-world tribological contacts. Boundary lubrication conditions were chosen in order to assess the IL's contribution in terms of friction and wear reduction. The additives showed very interesting properties, particularly in terms of surface protection: [C_6mim][TfO] 2%PEG allowed for a decrease in wear up to ~76% and [C_6-4-pic][TfO] 2%PEG up to ~46% when comparing to neat PEG 200. We hypothesize, based on XPS analysis of the contacting surfaces, that these ILs are surface active and readily adsorb to the steel surface, forming protective tribofilms that reduce wear under boundary regime.

The relevance of these results derives from the possibility of using these IL mixtures as competitive greener alternatives to commercial lubricants as they significantly reduce wear of bearing steel moving parts, allowing for great savings in replacing damaged parts.

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Potassium-based deep eutectic solvents as electrolytes for supercapacitors

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The need to look for energy storage systems is increasing day by day, and this is due to the necessity to improve the energy efficiency, reliability, and flexibility of electrical systems. For this reason, it is important to start looking for new and alternative energy sources [1]. Supercapacitors capture a great attention because of their high-power density, long life cycle, short charging time and the fact that they are more economical and environmentally friendly than traditional batteries. As it is known, supercapacitors require electrodes and electrolytes to work, and for what regards electrolytes, the main used are aqueous-based solvents, organic and now, the ultimate alternative is to use DESs (*DEEP EUTECTIC SOLVENTS*), which are formed from a eutectic mixture of Lewis or Bronsted acids and bases. DESs are easier to synthesize by mixing cheaper raw materials with good biocompatibility, they have higher stability windows and good conductivities. Unluckily, the potential application of DESs as electrolytes has not been investigated in sufficient detail, although new compounds have been studied, and also the possibility to use different metal ions than Li has occurred. An alternative that has started to be studied is Sodium, Na, and Potassium, K, too, since there's a major abundance of Na and K and they are way cheaper than Li. This work will be based on the research and study of new electrolytes, mostly potassium-based deep eutectic solvents. The study will start from the synthesis of the salt that is going to be used as a Hydrogen bond donor in the formation of the DES; after, there will be the formation of the DES by mixing the acid and the salt (in this case the acid will be hexanoic acid and the salt potassium hexanoate). Later, what should be one of the focuses of this study is the effect of water and salt content on some electrochemical properties. In particular, once the DES solutions will be ready, there will be studies regarding conductivity, viscosity, voltage window, and also analysis regarding the capacitance that these electrolytes could give to the supercapacitor.

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P87

Lignin modified titanate nanotubes for incorporation in sunscreen products

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Due to climate change and environmental degradation climate, the raising up of the UV radiation that reaches the Earth, is nowadays a global problem that urgently needs to be addressed to not compromise (further) future generations. Therefore, it is urgent to search for new materials, with UV-filter properties suitable for use as shields/protectors against UV radiation. Indeed, the use of nanoparticles in the cosmetic industry, especially sunscreen products, is very common, due to the safety of nanomaterials when in contact with human skin. Nanoparticles are unable to penetrate the human skin and cannot reach bloodstream [1].

In this context, the idea of this work is to prepare new hybrid titanate nanotubes (TNTs), and test them to slow down, or to effectively suppress the (undesirable) photo-oxidation of organic matter, when submitted to UV-visible radiation. After use as protective shields, their known photocatalytic properties, for pollutants removal, will contribute to making their discharge in the environment more sustainable.

Experimentally, in this work, the synthesis of TNTs nanoparticles, was performed by hydrothermal treatment of an amorphous precursor, previously prepared using $TiCl_3$ [2]. After, the nanoparticles were modified with distinct types of lignin, to give them photo-protective properties. The characterization of the pristine and modified nanoparticles was attained using XRD, TEM (Figure 1) and DRS. The modified TNTs were tested as catalyst to retard the photo-oxidation of a model molecule, under visible radiation. Afterwards, the same hybrid samples were incorporated in commercial sunscreen product and tested on several substrates, aiming to simulate human skin. An enhancement on the photo-protective efficacy of the commercial cosmetic products due the incorporation of modified TNTs was observed. The influence of several experimental parameters was evaluated and the results will be presented and discussed.

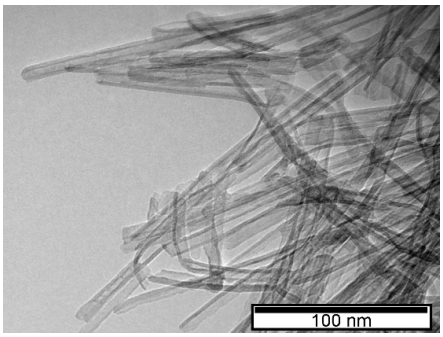

Figure 1. TEM image of the prepared TNTs.

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P88

Selective dissolution and reprecipitation of mixed plastic waste: development of sustainable solvent systems

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The recyclability of polymers is of crucial importance in the present days, considering the amount of primary plastic waste generated worldwide. The packaging sector generates the largest share of plastic waste, having produced over 15 million tons in 2020, according to the Eurostat Statistics [1]. Usually, this type of waste consists of a mix of various polymers and therefore its mechanical recycling is challenging, as it has low yield, high energy consumption and CO_2 emissions, resulting in a lower quality and uneven end products. Thus, a more efficient approach to this problem is needed. The selective solubilization of each polymer in a specific solvent without solubilizing the remaining ones is a good approach, as this strategy has a high yield of both polymer and solvent, since they can then be simultaneously recovered by precipitation using an antisolvent. This approach results in the recovery of each polymer with high purity and almost no changes from the original material [2]. Nevertheless, this strategy still makes use of organic volatile solvents that make the process environmentally unsafe and health hazardous, making the development of greener and more sustainable solvent systems a subject of increased relevance.

The design of these polymer-solvent-antisolvent systems needs to take into account the interactions of the polymer with the solvent and the antisolvent, as well as the solubility of both components, a key factor for obtaining a pure polymer, without solvent contaminations, and for the efficient recovery of the solvent, allowing it to be reused. The here proposed recycling process of water bottles, uses NADES (natural deep eutectic solvents) composed of terpenes (carvacrol and thymol) [3] as well as terpenes that are liquid at room temperature (limonene) to the target solubilization of PET and HDPE from water bottles and water bottle cap, respectively. PET was reprecipitated using ethanol as antisolvent, and water to allow the recovery of the pure solvent from the mixture. The aforementioned antisolvent is also suitable for the recovery of HDPE, as well as several mono, di, and tri alcohols. The individual polymers and respective solvents were recovered efficiently, showing similar thermal properties and FTIR spectra to the originals. Further analyses regarding the molecular weight and the crystallinity of the polymers were also carried out. The method also showed potential to selectively dissolve each polymer allowing to recover both polymers separately with high yield, as well as to recover the solvents without further need for purification.

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Hybrid materials based on polydopamine and WO_3 nanoparticles for pollutants removal

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Considering the time we live in, it is increasingly important to find solutions to the environmental problems that have been causing, such as contamination of water resources with high loads of heavy metals [1].

The design of novel architectures combining semi-conducting photocatalytic nanomaterials, namely WO_3 [2], and adhesive polymers with recognized adsorbent properties are promising for pollutants removal [3].

In this work, we coat glass substrates (fibers and slides) with polydopamine (PDA) film, which can be easily obtained through the oxidation of its monomer, dopamine. Two oxidants have been studied (O_2 and KIO_4) with the purpose of preparing adherent, uniform, and reproducible PDA polymeric coatings. Atomic force and scanning electron microscopies reveal faster formation, higher roughness and thickness, but lower surface adhesion for films prepared with KIO_4, in comparison with those formed in the presence of O_2 [4].

The WO_3 nanoparticles (NPs) used for PDA functionalization were synthesized from Na_2WO_4 solution at pH 1, under solvothermal conditions at 120 ºC for 48 hours. The prepared crystalline NPs have a lamellar shape with a width of about 10 nm, as confirmed by transmission electron microscopy and X-ray diffraction. The band gap energy value was estimated by diffuse reflectance spectroscopy, revealing the suitable properties of the semiconductor WO_3 NPs to be used in photocatalysis, under visible radiation. The novel hybrid materials were finally prepared by combining the PDA-modified glass fibers (or plates) with drop-cast or adsorbed WO_3 NPs, and their adsorbent and photocatalytic reduction performance successfully carried out towards the removal of chromium VI from aqueous solutions.

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Regeneration of activated carbons exhausted with pharmaceuticals

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There is an increasing use of activated carbon-based technologies for a more effective control of contaminants of emerging concern, in particular pharmaceutical compounds (PhCs). These technologies are mainly applied in wastewater treatment plants where carbon materials are used in the form of powdered or granular activated carbons (PAC and GAC, respectively). While due to limited PAC recovery options they are mainly applied in single-use processes, GAC are applied in column filters and once exhausted can be easily recovered and regenerated. The performance of GAC for PhCs removal from water is dependent on the adsorbent (GAC), adsorbate (PhC) and water matrix [1] thus it is important to address the major factors influencing the regeneration process aiming to identify the PhCs properties (e.g., polarity, solubility, pH and molecular structure) that allow to predict the regeneration efficiency on a PhC exhausted GAC. In the present work the effectiveness of thermal regeneration methods of GAC exhausted with PhCs was assessed using a commercial GAC exhausted with sulfamethoxazole (SMX), paracetamol (PARA) or caffeine (CAF) at pH 5, performing the thermal regeneration at 400 ºC under steam or N_2 flow. Figure 1 shows how the regeneration efficiency (RE) depends on both the regeneration atmosphere and PhC. SMX exhausted GAC presented the lowest RE while CAF has the highest, regardless the cycle and thermal regeneration was made under steam or N_2. Adsorption data shows the apparent higher affinity of SMX for the GAC which may explain this behavior [2]. Given the complex speciation of SMX complementary assays are being performed at pH 7.6 (pH of effluent in wastewater treatment plants) to evaluate if the anionic SMX specie have a distinct adsorption and regeneration profile compared to neutral SMX (specie present at pH 5).

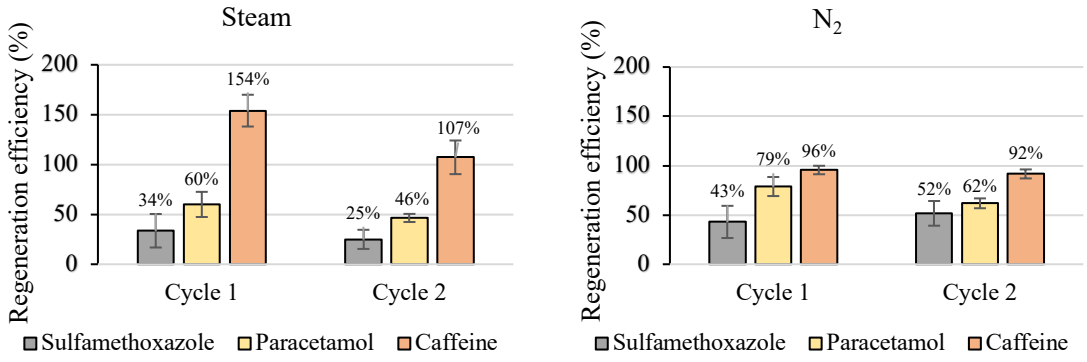

Figure 1. Regeneration efficiency of a commercial GAC exhausted with sulfamethoxazole, paracetamol and caffeine, using different thermal regeneration under steam or N_2 flow.

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Objective assessment of microplastic contamination trends of a vast coastal area

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The environmental pollution by microplastics is well recognized. Microplastics were already detected in various matrices from distinct environmental compartments worldwide, some from remote areas. Various methodologies and techniques have been used to determine microplastic in such matrices, for instance, sediment samples from the ocean bottom. In order to determine microplastics in a sediment matrix, the sample is typically sieved through a 5 mm mesh, digested to remove the organic matter and density separated to isolate microplastics from the denser part of the sediment [1]. The physical analysis of microplastic consists of visual analysis under a stereomicroscope to determine particle size, colour, and shape. The chemical analysis is performed by an infrared spectrometer coupled to a microscope (micro-FTIR), allowing the identification of the chemical composition of microplastic, *i.e.*, the type of polymer.

Creating policies and legislation to control and manage (micro)plastic pollution is essential to protect the environment, namely the coastal areas. The developed regulation must be supported by the known relevance and trends of the pollution type.

This work discusses the assessment of contamination trends of a 700 km^2 oceanic area affected by contamination heterogeneity, sampling representativeness and the uncertainty of the analysis of collected samples [2]. The methodology developed consists of objectively identifying meaningful variations of microplastic contamination by the Monte Carlo simulation of all uncertainty sources. This work allowed to unequivocally conclude that the contamination level of the studied area did not vary significantly between two consecutive years (2018 and 2019) and that PET microplastics are the major type of polymer. The comparison of contamination levels was performed for a 99% confidence level. The collected information on the environmental area is crucial for the objective and binding determination of microplastic contamination relevance.

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P92

Hybrid materials based on solar-active semiconductor nanoparticles and fibres for photocatalytic degradation of pollutants

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Water pollution is one of the most pressing sanitation issues. Many countries lack wastewater treatment systems, which can lead to public health problems. In addition, emergent pollutants removal can become problematic and costly due to intense human activity [1]. Photocatalysis, Figure 1, an advanced oxidation process, using semiconductor nanoparticles (NP) is considered a promising technology capable of breaking down different types of organic pollutants under the influence of light [2]. This approach allows to clean up polluted water with a lower cost.

In this work, hybrid materials based on visible light active NP such as bismuth oxychloride (BiOCl) and fibres (glass and polyester) are used for pollutants removal by photodegradation under solar irradiation. Crystalline and small sheet-shaped BiOCl NPs are obtained as confirmed by XRD and SEM analysis. The self-sensitizing properties of BiOCl [3] overcome its large bandgap ($E_g \approx 3.3$ eV) which is estimated by DRS. The *in situ* glass and polyester fibres modification with the NPs is achieved by hydrolysis at room temperature. The hybrid materials are characterized by DRS and SEM corroborating the presence of the NPs on the fibre surface.

The photocatalytic degradation of caffeine is used to compare the performance of the hybrids and to optimize the operation of the scale-up reactor. Several parameters are tested, including pollutant concentration, type of fibre, hybrid/solution volume ratio, immersion depth and flow speed.

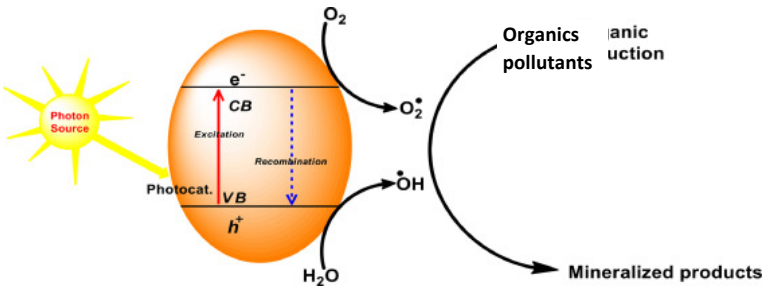

Figure 1. Schematic illustration of the photocatalytic process using semiconductor materials.

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P93

Synthesis and Characterization of CA/SiO2 and CA/SiO_2_UIO66 Membranes for Hemodialysis

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Hemodialysis is a clinical membrane based treatment for the extracorporeal removal of blood toxins. The current study focuses on the synthesis and characterization of ultrafiltration (UF) mixed matrix membranes for small water soluble toxins removal.

Mixed matrix membranes of cellulose acetate (CA) and Silica - CA/SiO_2 - were synthetized by coupling the wet phase inversion technique and the sol-gel method[1]. Other set of CA based membranes were synthesized by direct mixing of the metal organic frame work (MOF) - UiO-66 - in the casting solution of the CA/SiO_2.membranes. CA and CA/SiO_2 membranes were subjected to post-treatment described by da Silva *et al.*[2] by using the following surfactant solutions: an aqueous solution of 20 % glycerol (G20) ,an aqueous solution of triton-X-100- and glycerol (GT).

Permeation experiments were carried out in an ultrafiltration set-up for the CA, CA/SiO2, CA_UIO66; CA/SiO2_UIO66 and CA/SiO2_G20.membranes to assess their permeation characteristics in terms of hydraulic permeabilities, molecular weight cut-off (MWCO), and apparent rejection coefficients to NaCl, Na_2SO_4 ,urea, and p-cresyl sulphate.

In order to rationalize the previous results, physical properties of the membranes were investigated by Differential Scanning Calorimetry (DSC) and Dielectric relaxation spectroscopy (DRS). The former allowed determining parameters such as the crystallinity degree and the glass transition temperature (T_g). On the other hand, DRS was used to analyze the molecular dynamics of each of the CA based membranes in the sub-T_g temperature region [3]; the different relaxation processes detected were interpreted taking into account the interactions of each CA based membrane with water, glycerol and triton-X-100 present as a result of the applied post-treatment.

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P94

Solar-driven Calcination of Natural Limestone and Marble Wastes for Calcium Looping Processes

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The Ca-Looping (CaL) is one of the most promising technologies for post-combustion CO_2 capture [1,2] and thermochemical energy storage [3] based on the following reversible chemical reaction: CaO (s) + CO_2 (g) ⇄ $CaCO_3$. Despite the advantages of CaL, i.e., high CO_2 sorption (0.78 g CO_2/g CaO), high energetic density (1790 kJ/kg $CaCO_3$), availability and low price; the energy consumption for the $CaCO_3$ regeneration at high temperatures (> 900 ºC) is still pointed out as a considerable drawback. Concentrated solar technology (CST) for CaL consists of using the high temperatures attainable with CST to drive an endothermic chemical reaction and allows overcoming this issue.

In this study, the calcination efficiency of different $CaCO_3$-based materials is compared using a laboratory scale solar directly irradiated fluidized bed reactor (S-FBR) and a conventional fluidized bed reactor heated by an electric oven (C-FBR). The Solar-driven calcination experiments were carried out in a S-FBR on a vertical-axis medium-size solar facility of 1.5 kW at PROMES-CNRS laboratory, during an access campaign within the framework of the SFERA-III European project SolMat4TCES. Four limestones and three different marble wastes were tested, and the calcination efficiency was evaluated for the effect of: (i) average particle sizes (250-355 µm and 355-500 µm); (ii) duration time of calcination (15 min vs 30 min); (iii) fluidizing gas atmosphere (air at 800 ºC vs 50% of CO2 at 900 ºC and 930 ºC), and (iv) inert dark additive SiC (20% and 40% (w/w)) to improve the solar absorptance and thermal conductivity. The same procedure was carried out using the C-FBR and the results are compared. The initial properties of the materials and their changes after calcination, were monitored using several characterization techniques: XRD, N_2 adsorption, UV-Vis-NIR spectroscopy and TGA.

The results show that all the samples of natural resources and wastes of $CaCO_3$-based materials were successfully calcined in the S-FBR at PROMES-CNRS. The calcination efficiency is higher for 30 minutes calcination time than for 15 minutes, and is higher for the smaller particle sizes, in agreement with the results obtained in the C-FBR. The calcination efficiencies obtained at the S-FBR and C-FBR are comparable and in most of the experiments, high values within the range of 80% -100% were obtained. This study, using solar radiation as source of energy, emphasizes the viability of integrating CSP and CaL for TCES or CO_2 capture processes.

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P95

Production of astaxathin nanoparticles using the supercritical antisolvent precipitation process

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Astaxanthin is a red carotenoid with many important biological properties, such as anti-oxidant and anti-inflammatory, which make it reliable to nutraceutical, food, cosmetic and pharmaceutical industries. This carotenoid is also believed to play an important role in the protection against a great number of chronic and acute health conditions, DNA damage prevention, macular degeneration and cancer treatment [1,2]. The use of astaxanthin as colorant and anti-oxidant is enhanced if smaller particles are used, since the colour properties of the pigmented system are improved. Also, with smaller particles it is possible to obtain more stable emulsion, as well as increase *in vivo* solubility and bioavailability of the carotenoid.

Particle design is a subject increasingly discussed nowadays and with extreme importance for compounds to be used in the nutraceutical, cosmetic and pharmaceutical industries. The properties of a biopharmaceutical compound, such as bioavailability, solubility, dissolution rate and formulations stability are directed influenced by particle size [3].

New approaches for the production of nanoparticles, such as supercritical antisolvent micronization process (SAS), are now catching the interest, presenting as a viable solution when compared with the traditional techniques [4].

In the present work a factorial design was investigated for the micronization of synthetic astaxanthin by the supercritical antisolvent technique (SAS). The objectives were accomplished using CO_2 as antisolvent and THF as solvent. Design of experiments was applied in a fractional factorial design at 4 factors, pressure (100 to 150 bar), concentration (0.5-3 mg/ml), temperature (40-60°C) and solution flow rate (0.5-1.5 ml/min) and at 2 responses (yield of micronized product and mean particle size). Screening analysis showed higher significance to pressure, concentration, and temperature. Two experiments were run in order to assess the temperature effect. It was verified that temperature influenced the morphology of the micronized particles and that at higher temperatures smaller particles with a sphere like morphology were obtained. Central Composite Design (CCD) was used for optimization of the process. The evaluated factors were pressure (100-150 bar) and concentration (1-3 mg/ml), being the mean particle size of the micronized compound the response. Minimum mean particle size obtained was 0.182 µm at 100 bar, 60° C, 0.5ml/min and 3 mg/ml. This result is in agreement with that predicted by the CCD.

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Treatment of effluents containing hexavalent chromium by electroless precipitation on polyaniline films

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Electroless precipitation is a metal ion reduction process carried out by some conductive polymers containing nitrogen atoms. It consists in a spontaneous reduction process, without using an electrical source of energy, exclusively of ions with a high potential reduction potential [1].

The objective of this work is to study the performance of polyaniline films in the electroless precipitation of hexavalent chromium. These films were electrosynthesized on graphite electrodes in potentiodynamic mode.

Three polyaniline films were synthesized, all of them with the same number of cycles and the same sweep rate (50 cycles at 20 mV/s). The only variable was the type of electrode where the film was formed. Graphite electrodes with different porosities were used in order to select which one produced a more reliable film with higher electroactivity, that reduced a greater amount of hexavalent chromium.

The thickness of the film and their dielectric properties were accessed by ex-situ ellipsometry using a conventional three phase model in a multi incident angle approach.

To evaluate the performance of polyaniline films in the reduction of Cr^{VI} to Cr^{III}, samples collected during electroless precipitation were complexed with 1,5-Diphenylcarbazide (DFC) and analyzed by UV-Vis spectroscopy [2].

Finally, in order to examine the robustness of the polymer, reuse trials were made with the film that had revealed the best reduction efficiency. With these tests it was possible to determine the number of times that polyaniline was able to reduce hexavalent chromium without losing its properties and compromising its efficiency [2].

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Sustainability of chitin and chitosan extraction

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Chitin is one of the most abundant biopolymer in nature and it can be found in the exoskeleton of crustaceans, insects, and fungi. Chitosan is mainly obtained by deacetylation of chitin and it has been studied for its promising applicability.

Chitin and chitosan are both biodegradable, non-hazardous, and non-toxic. They have been recognized for their potential role in biomedical, cosmetics, food industry, and wastewater treatment.

In the past years, the traditional form of extracting chitin, chemical extraction, has been studied because it is related to some environmental disadvantages and issues.

Recently, a variety of new methods more “green” have been created and developed in the way of increasing the sustainability of the chitin extraction process.

These green extraction techniques such as biological extraction, enzyme-assisted extraction, and microwave-assisted extraction, meets several green metrics that are already established.

Despite these new promising methods, the evaluation of the upscalability at the industrial level requires more investigation.

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Ru/Zeolites synthesis for Sabatier reaction: The influence of thermal decomposition conditions on the performances

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Over the past decades, the intensive utilization of non-renewable energy resources such as fossil fuels led to an increase of the CO_2 emissions in the atmosphere, being responsible for human-induced climate change. Therefore, different strategies have been studied in order to reduce and control CO_2 emissions, namely CO_2 capture and storage or its conversion into useful chemicals and fuels. In this scenario, conversion of captured carbon dioxide into fuels using green hydrogen produced via water electrolysis with renewable energy refers to Power to Gas (PtG) concept. Among the possible CO_2 utilization routes, its conversion to CH_4, as a substitute to natural gas, via Sabatier reaction has gained interest. Synthetic natural gas (SNG), which demand has steadily increase, is considered a clean energy and an interesting energy vector, since it can be directly injected into already existed natural gas grid [1].

Taking into account that CO_2 is a very stable molecule and the exothermicity of this reaction, innovative and stable catalysts are needed to achieve adequate CO_2 conversion and selectivity towards CH_4. Active metals such as Ni and Ru supported on different metal oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2, CeO_2) have been investigated for this reaction [2]. However, Ni-based catalysts still present some challenges as instability, sintering and deactivation in presence of oxygen in real effluents. In this way, Ru is presented as an alternative with higher activity, due to the strong ability to activate CO_2 and dissociate H_2, providing a decrease in the reaction temperature. Although its higher cost, Ru is more resistant than Ni in oxidizing atmospheres, it shows a higher sulphur tolerance, and carbon deposition and sintering are both inhibited. In spite of Ru catalysts interest for Sabatier reaction, further research is still required for improving the physicochemical properties of these systems in order to maximize the catalytic performances.

In this work, the influence of the preparation conditions on the synthesis of Ru/Zeolite catalytic systems was assessed. For this purpose, a series of 3 wt.% Ru catalysts supported over an optimized USY zeolite were synthesized by incipient wetness impregnation. Afterwards, samples were thermally treated for Ru precursor salt decomposition following different conditions, including oxidative and reductive atmospheres. The prepared catalysts were characterized with several advanced techniques (e.g., XRD, TGA, H_2-TPR, N_2 adsorption, TEM) and tested towards CO_2 methanation in a micro catalyst bed unit (250 to 450 ºC, 5 bar).

Results showed that the preparation conditions affected mainly the Ru^0 particle size and its dispersion on the zeolite surface, while the textural and structural properties of the materials were not significantly influenced by this parameter. Indeed, the sample prepared following a reductive atmosphere procedure showed an enhanced catalytic performance (~81 % CH_4 yield at 325 ºC), attributed to an increase of Ru^0 particle size and metal dispersion (< 6 nm and 9 %, respectively).

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Effect of solvent and heat treatment conditions on TiO_2 and TiO_2@PAC properties

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Photocatalysis is a promising water treatment technology, and among catalysts, nanosized semiconductor particles have met superior catalytic properties. TiO_2 is the most popular photocatalyst due to its unique properties, but its performance is highly dependent on the crystalline structure and on the particle size. The major bottleneck of nanosized semiconductors use in full-scale wastewater treatment is related to post-separation and aggregation issues. Powdered activated carbon (PAC) are high performance adsorbents with proven effectiveness in water treatment and are also considered ideal supports to overcome TiO_2 aggregation problems with the advantage of improving pollutants/catalyst contact, minimizing electron-hole recombination and help harvesting solar spectrum [1].

The TiO_2 nanoparticles were prepared by two methods: sol-gel method using titanium butoxide as precursor [2] and a swift chemical route that is an extension of the hydrothermal process that uses $TiCl_3$ as titanium precursor [3]. The sol-gel method was performed with different water:isopropanol volume ratios (1:20 or 20:1) and for sol-gel protocols the post-treatment effect was also evaluated: heat treatment at atmospheric pressure (Atm) at 250 ºC during 24 h or hydrothermal treatment (HT) at 200 ºC during 6 h. After, the TiO_2@PAC composites were prepared by adding the desired amount of a commercial PAC during TiO_2 synthesis. So far, the materials – TiO_2 and TiO_2@PAC – were characterized by XRD, N_2 adsorption at -196 ºC and DRS. The decolorization of methylene blue aqueous solution under UV light has been used as photocatalytic model reaction.

The configuration of N_2 adsorption isotherms of TiO_2 nanoparticles is highly dependent of the experimental parameters used during synthesis (Figure 1). The TiO_2 produced using the high level isopropanol during sol-gel synthesis and submitted to hydrothermal treatment is the sample presenting the highest BET surface area m^2/g), contrasting with the value obtained for the sample starting from $TiCl_3$ precursor (67 m^2/g). data reveal the presence of anatase phase for all materials. Preliminary results indicate that the nanocomposites TiO2@PAC prepared using sol- method with high level of isopropanol and heat treatment at Atm or HT have promising photocatalytic performance for methylene blue discoloration.

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XRD

TiO_2

gel

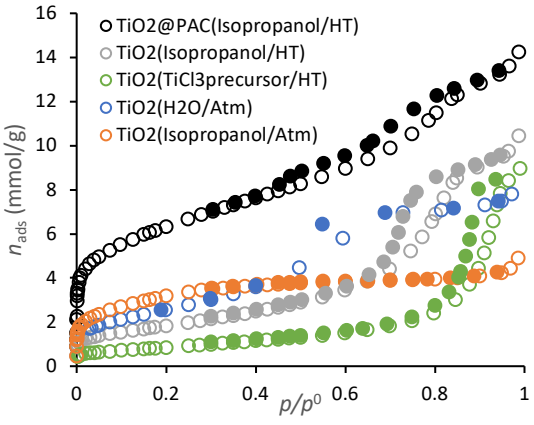

Figure 1. N_2 isotherms at -196 ºC.

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Iron(II) Organometallic Complexes With Imidazole-based Ligands as ABCB1 Inhibitors

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Cancer is one of the leading causes of death in the world today,[1] reinforcing the need to develop new, more selective, and effective treatments that address the problems associated with the available treatments. Based on our previous good results obtained for cationic Fe-Cp complexes against a wide variety of tumor cell lines,[2] a new family of compounds with the general formula [Fe(η^5-C_5H_5)(CO)(PPh_3)(Imi-R)][CF_3SO_3], where Imi-R are imidazole-based ligands, was recently developed.[3] All compounds were fully characterized by common spectroscopic techniques (NMR, FT-IR, UV-Vis, X-Ray diffraction of monocrystal) and their purity was confirmed by elemental analysis. All compounds crystallize into centrosymmetric spatial clusters in a typical “piano stool” distribution. Given the growing importance of finding alternatives to overcome different forms of multidrug resistance, all compounds were tested against cancer cell lines with different expressions of the ABCB1 (P-gp) efflux pump: human colon adenocarcinoma cells Colo205 and P-gp expressing Colo320. Compound 3 (Imi-R = 1-benzylimidazole) stood out as it was the most active in both cell lines. Complementary studies via rhodamine 123 fluorometric accumulation assay and through iron cellular accumulation studies by ICP-MS and ICP-OES methods revealed that compounds 3 and 2 (Imi-R = 1*H*-1,3-benzodiazole) exhibit a very potent P-gp inhibitory effect, especially compound 3.

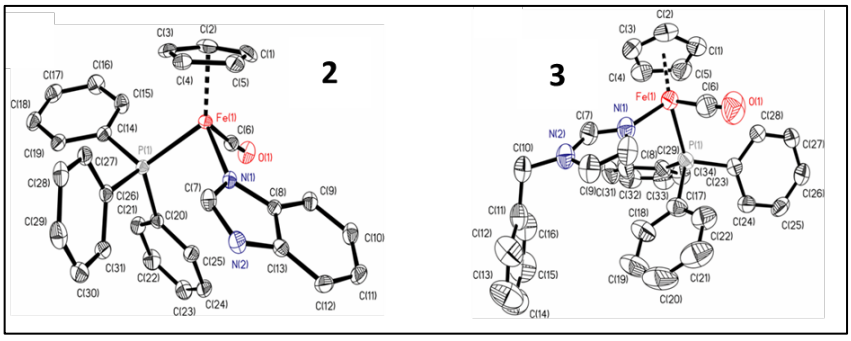

Figure 1. ORTEP for the cations of compound 2 and 3. Hydrogen atoms are omitted for clarity.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A. P. thanks FCT for his Ph.D. Grant (SFRH/BD/139412/2018 and COVID/BD/153267/2023). A.V. acknowledges the CEECIND 2017 Initiative (CEECIND/01974/2017).

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P101

Fluorescent Homooxacalixarene-Based Receptors: Recognition of Anions and Nitroaromatic Compounds

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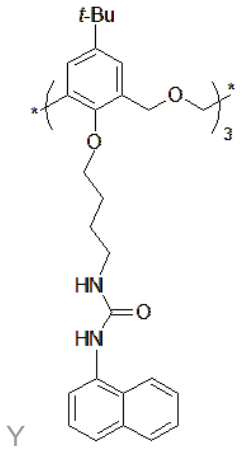
Anion recognition by synthetic receptors continues to attract much attention, as anions play essential roles in numerous biological systems and environmental processes [1]. By other side, the development of chemical sensors for the detection of explosives is a major task in the fight against terrorism and in homeland security. Fluorescence-based methods are among the analytical techniques more used in sensing of nitroaromatic compounds (NAC's), such as trinitrotoluene (TNT), dinitrotoluene (DNT) and trinitrophenol (TNP). The versatile macrocyclic compound calixarenes bearing fluorophoric groups have been widely studied in the recognition of both kind of analytes [2].

In the course of our studies on binding properties of ureido-homooxacalixarene derivatives, we have extended our research into the study of fluorescent receptors for anions and nitroaromatic compounds [3-5]. This work reports the affinity of compounds **1** and **2**, bearing naphthylurea groups on the lower rim, towards several relevant anions and also selected nitroaromatic explosives. These studies were performed by proton NMR, UV-Vis absorption and steady-state fluorescence titrations.



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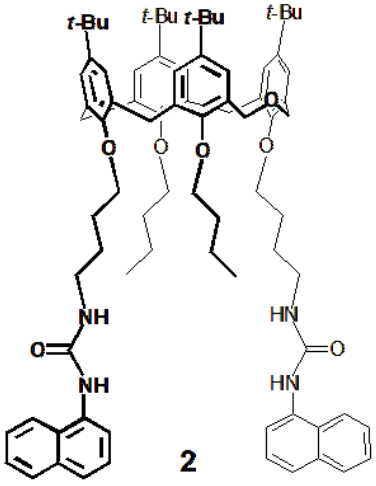

2

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A. S. Miranda thanks a PhD Grant ref. SFRH/BD/129323/2017 and COVID/BD/152147/2022.

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P102

3D printed leucite/zirconia dental materials with antibacterial properties

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Zirconia (ZrO_2) is a highly used material for dental restorations due to its ability to withstand high loads during mastication without fracturing. Besides, it induces minimal wear on opposing teeth. The usual practice of coating zirconia restorations with glaze to improve their optical properties can lead to increased wear on the opposing teeth due to the fragile nature of the coating. To overcome this issue, the production of glass-ceramic composites may become a good alternative. Although subtractive manufacturing is the most used technique to produce dental materials, 3D printing has been emerging as an alternative technology and so far, there are some works in the literature that show that it presents innumerous advantages and can successfully produce materials with suitable properties for dentistry.
In this work, samples of leucite reinforced with 12.5%, 25% and 37.5% (%wt) ZrO_2 were produced by robocasting and characterized in terms of mechanical and tribological properties. Additionally, the application of an antibacterial coating (silver diamine fluoride (SDF) + potassium iodide (KI)) over the best performing material was evaluated.

The results showed that the highest values for both microhardness and fracture toughness were obtained for 25% ZrO_2, followed by 37.5% ZrO_2, and then by 12.5% ZrO_2. More, 25% ZrO_2 induced the least wear on the antagonist cusps and was the less worn material. It was also observed that 25% ZrO_2 presented a superior performance compared the currently used zirconia coated with glaze: in fact, it led to lower cusps' wear and higher translucency. Finally, it was found that the SDF+KI coating over the 25% ZrO_2 samples hampered *Staphylococcus aureus* adhesion and proliferation.
In conclusion, robocasting has the potential to produce leucite/zirconia materials. 25% ZrO_2 revealed to be the most effective formulation in terms of microhardness, fracture toughness, and prosthesis/cusps wear. Furthermore, the results suggested that the SDF+KI coating can potentially be used as an effective antibacterial coating in dental restorative materials.

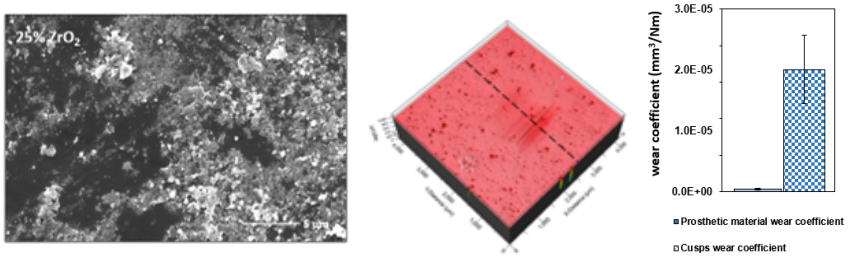

Figure 1. (A) SEM images of the cusps, (B) Profilometer image of 25% ZrO_2 and (C) Wear coefficient of cusps and 25% ZrO_2, after wear tests.

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P103

Structural Optimization of Alkyl Deoxyglycosides with Antibacterial Activity in Gram-negative Bacteria: Synthesis of Fluorinated Derivatives

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The investigation of new antimicrobial agents with innovative mechanisms of action against multidrug-resistant Gram-negative bacteria is a top public health priority [1], with carbohydrates exhibiting a vast potential for successful antibiotic drug discovery [2]. In a very recent proof-of-concept study, we have demonstrated the bactericidal activity of sugar-based leads **1** and **2** (**Figure 1**) against carbapenem-resistant Gram-negative isolates of clinical importance, when combined with subtherapeutic concentrations of colistin [3]. As part of our structural optimization plan for these compounds towards improved antibiotic activity and reduced toxicity, we herein focused on the design and synthesis of deoxyfluorinated lead analogues based on the well-established importance of fluorinated molecules in Medicinal and Pharmaceutical Chemistry [4]. Owing to the highly electron-withdrawing properties of the fluorine atom, the selective bioisosteric replacement of hydrogen with fluorine atoms is expected to render new molecules with (i) enhanced membrane permeation; (ii) fluorine-promoted changes in dipolar interactions with potential for improved binding affinity to the biological target; and (iii) improved metabolic stability, among other advantages [4]. In this communication, we will disclose our latest results on regioselective DAST-promoted sugar deoxyfluorination, as well as optimized *O*- and *C*-glycosylation reactions towards the synthesis of new lead analogues (**Figure 1**) for future biological evaluation in combination with colistin against carbapenem-resistant Gram-negative bacteria.

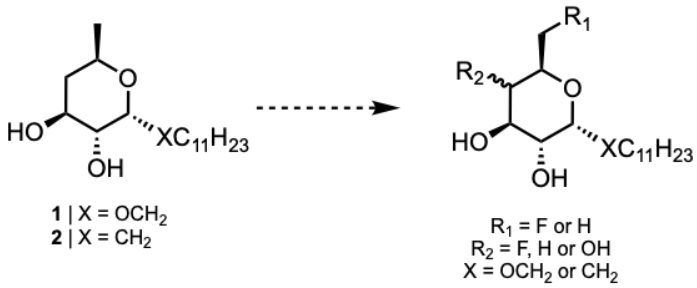

Figure 1. Lead analogues and target molecules.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. Mpanzu Nelo would like to acknowledge Instituto Nacional de Gestão de Bolsas de Estudo de Angola (INAGBE-Angola) for his Ph.D. grant. Ana Marta de Matos wishes to thank FCT for funding through the Individual Call for Scientific Employment Stimulus (2022.07037.CEECIND).

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P104

New hit compounds towards cancer – assessing the chemical repertoire

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Cancer has been long known to be one of the leading diseases in the number of deaths. Despite all advances in cancer treatment and increased survival rate in past few decades, only in Europe in 2020 were reported around 4 million new cases and 1.9 million deaths [1].

One of the compounds that potentially can be used towards a cancer treatment is natural alkaloid chelerythrine [2]. Chelerythrine is already known to have an anti-proliferative effect on some cancer cell lines inhibiting their growth and division. In this frame, chelerythrine was tested on prostate (LNCap), T-cell leukemia (Jurkat) and multiple myeloma (MM.1S) cell lines. The cell viability was measured by resazurin assay in 96-well plate with a cell suspension at a density of 5×10^5 cells/mL for Jurkat and MM.1S and 2×10^5 cells/mL for LNCap. Chelerythrine exhibites an anti-cancer effect with IC_{50} values less than 10 μM for chosen cell lines which is comparable to some drugs [3].

Moreover, three ruthenium scorpionate compounds were studied to exhibit anti-cancer activity against the same cell lines. It was found that one of them has a close to chelerythrine IC_{50} values which is promising for the further investigation.

In the future, the mechanism of their action against these cell lines will be studied as well by performing metabolomics and proteomics.

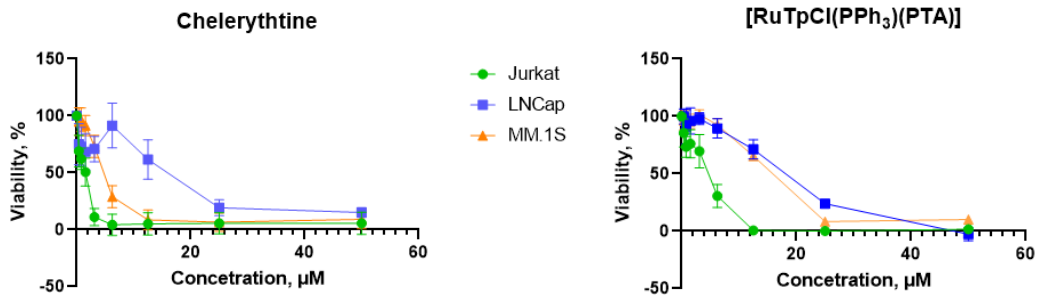

Figure 1. Dose response curves of chelerythrine and [RuTpCl(PPh3)(PTA)] for LNCap, Jurkat and MM.1S cell lines.

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P105

Irradiation-responsive polysulfone film as a colorimetric UVA/UVB differentiator

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A wearable, small size, flexible and energy consumable free colorimetric detector of UVA radiation and UVB/UVA differentiation was created based on the peculiar stimuli-responsive behaviour of an imidazolium based ionic liquid. Semi-transparent polysulfone films are transformed into opaque and homogenous red films under UVA radiation (315–360 nm), while lower wavelength exposure (280-315 nm) induces an increased emission detectable under dark light, with no colour modification of the film under visible light. Thermal analysis (TGA and DSC), spectroscopic analysis (FT-IR, 1H-NMR and UV-Vis), scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were conducted to elucidate confinement mechanism and irradiation effects [1].

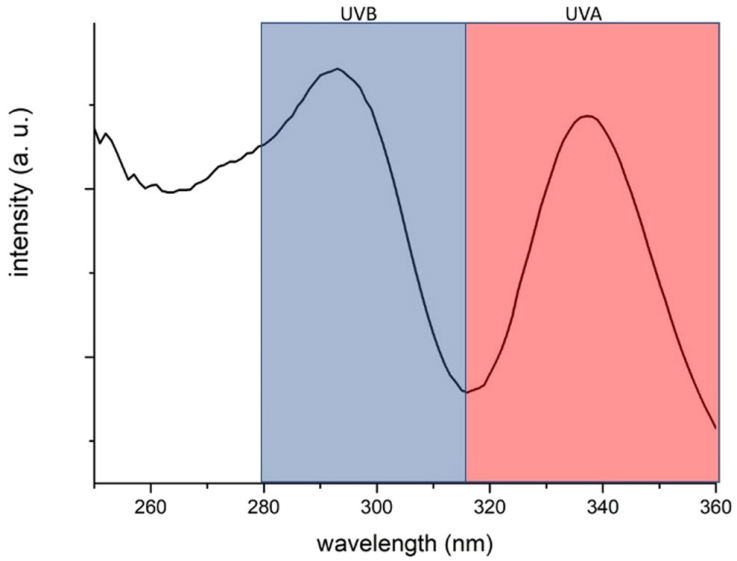

Figure 1. Excitation spectra of [C_2mim][fod] @PSU for the maximum emission band at 390 nm.

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References: [1] Bernardo Monteiro João P. Leal, Mani Outis, Maria H. Casimiro, Cláudia C. L. Pereira. *J. Mater. Chem. C* **2023**, 11, 5199–5207.

P106

Synthesis of New Curcuminoid Derivatives with Potential Antioxidant and Hypoglycemic Properties

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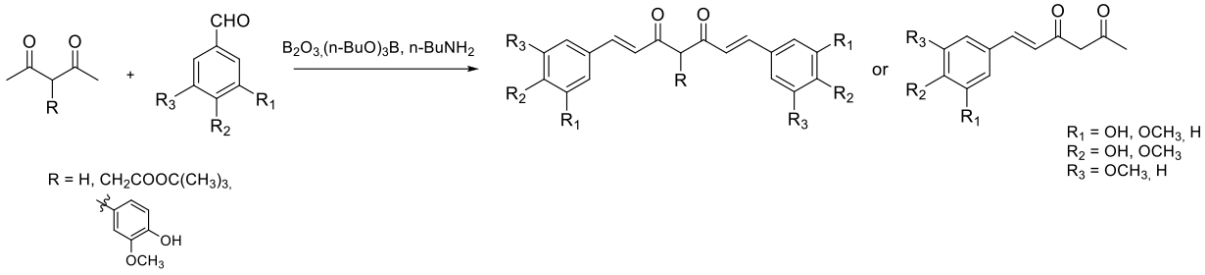
Curcumin is the principal constituent of turmeric i.e., the ground rhizomes of *Curcuma longa*. This compound has therapeutic and protective effects against a variety of diseases, including cancer, diabetes, neurological and cardiovascular diseases. Despite this, curcumin has low bioavailability during oral administration and low water solubility, which limits its clinical applicability [1]. Recent studies with diabetic rats suggest that substitution of the central position on the b-diketone chain leads to curcumin-based derivatives that potentiate the effects of curcumin, improving the fasting glucose and the endothelial function on type 2 diabetes [2].

This work is therefore based on the synthesis of curcumin analogues through the introduction of different groups in the main β-diketonic chain, the change of substituent groups in the aromatic rings or the formation of mono-curcuminoids, in order to improve both its biological properties, their bioavailability and solubility. The principal synthetic pathway is presented in scheme 1 and products were characterized by usual spectroscopic techniques and X-ray diffraction. Solubility tests in water were also carried out and the antioxidant capacities of the compounds were evaluated.



Scheme 1. General synthetic strategy for curcuminoid derivatives.

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References: [1] S. Gupta, S. Patchva, W. Koh, et al.; *Clinical* and Experimental *Pharmacology* and *Physiology* **2012**, 39, 283-299. [2] S. Oliveira, T. Monteiro, L. Henriques; *European Journal of Clinical Investigation* **2019**, 49, 125.

P107

Optical polymeric boron sensors for evaluation of permeability of gram-negative pathogens

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Antimicrobial resistance is considered one of the top global public health problems. In the recent years gram-negative bacteria have become resistant to antibiotics, resulting in high number of deaths [1]. Antimicrobial resistance annual epidemiological report for 2021 from European Centre for Disease Prevention and Control states that *Acinetobacter spp* resistance to antibiotics has increased for the second year in a row. In addition, this gram-negative bacterium is problematic because it can persist in the healthcare environment and is difficult to eradicate. Another gram-negative bacterium, *Klebsiella pneumoniae,* was also reported to have increased its resistance towards antibiotics [2].

In this work we aim to prepare optical polymeric boron sensors for application in the evaluation of permeability of gram-negative pathogens. For that, both homo- and copolymerization of 2-(diethylamino)ethyl acrylate with *N*-acryloxysuccinimide was achieved by photo-initiated reversible addition-fragmentation chain transfer polymerization. This controlled type of polymerization uses a chain transfer agent to prepare polymers with predictable molar mass, narrow chain length distribution and high end-group integrity [3]. We have obtained total conversion of the monomer to the homopolymer, with molecular weights between 30 and 70 kDa, depending on the polymerization conditions used. Polymerization kinetics and polymer characterization by NMR and SEC were performed.

Synthetic pathway for the boron sensor preparation started with a selected triphenylene derivative, which was chosen for its emission properties upon complexation with boron species in aqueous solutions [4, 5]. Optimization of some of the reaction steps is still in course to increase yields. We expect that upon bonding the boron sensor with the co-polymer, the resulting boron sensor can be used to evaluate the permeability of gram-negative bacteria.

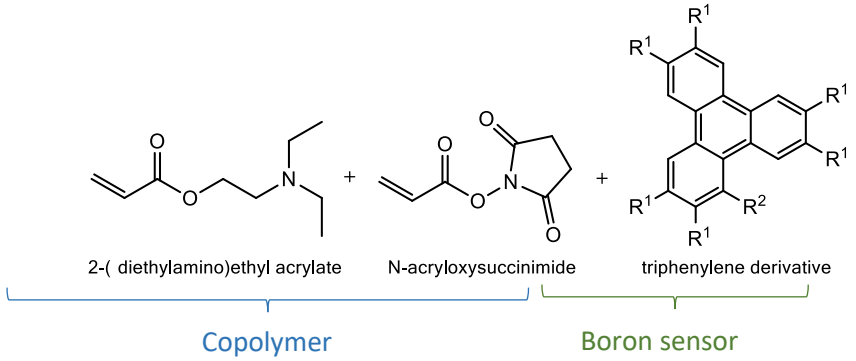

Figure 1. Organic building blocks used to prepare polymeric boron sensors.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

References: [1] S. I. Miller; *MBio* **2016**, *7*, 1-3. [2] European Centre for Disease Prevention and Control. Antimicrobial resistance in the EU/EEA (EARS-Net) – Annual Epidemiological Report 2021, Stockholm: ECDC; **2022**. [3] Favier, A; Charrevre, M. T.; *Macromol. Rapid Commun* **2006**, 27, 653-692. [4] S. Alves, C. Baleizão, J. P. S. Farinha, *Anal. Methods* **2014**, 6, 5450-5453. [5] L. Areias, S. Alves, A. P. da Costa, C. Baleizão, J. P. S. Farinha, *RSC Advances* **2017**, 7, 4627-4634.

P108

New ruthenium complex containing a monosubstituted 2,2'-bipyridine for the treatment of metastatic breast cancer

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Cancer is characterized by the uncontrolled growth of abnormal cells that can appear in almost all types of organs in the human body and can lead to possible proliferation, either locally or metastatically. According to the World Health Organization (WHO), cancer is the second cause of death worldwide, with 19.3 million of new cases and 10.0 million of deaths worldwide only in 2020. Breast Cancer is currently the most common and lethal type of cancer in woman with 4 new cases and 1 death by BC every single minute [1].

The main goal of current cancer therapies is to selectively kill tumour cells while avoiding any damage to healthy cells and tissues. Since this has been the limiting step of any therapy, chemotherapy continues to be regarded as the most viable option for treating cancer when surgery is not valid. In this context, our group has been working on the incorporation of the promising anticancer complex [Ru(η^5-C_5H_5)(PPh_3)(2,2'-bipyridine)][CF_3SO_3] (TM34) into metallodrugs delivery systems [2]. Although bipyridine ligands are extensively exploited in designing inorganic or organometallic complexes for medicinal applications, in particular for cancer, the use of monosubstituted 2,2'-bipyridines remains underexploited, mostly due to sparce commercially available options and difficult synthesis.

Herein, we disclose the synthesis and structural characterization (NMR, UV-Vis, FT-IR) of a novel 4-monosubstituted 2,2'-bipyridine, as well as coordination of this ligand to a ruthenium cyclopentadienyl complex, that will be used as the cytotoxic agent of a smart metallodrug delivery system [2].

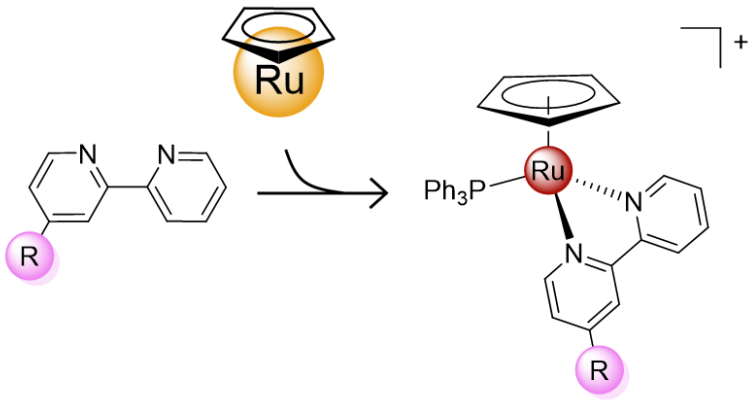

Figure 1. Strategy for the preparation of ruthenium complexes with a monosubstituted 2,2'-bipyridine ligand.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. T. S. Morais and J. A. S. Coelho thank FCT, as well as POPH and FSE-European Social Fund for Scientific Employment Stimulus Initiative for the projects CEECIND/00630/2017 (T.S.M.), 2022/00028/CEECIND (T.S.M.), and 2020/02383/CEECIND (J.A.S.C.).

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P109

Synthesis and pharmacological activity of novel bisquinolizidine derivatives

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Bisquinolizidine alkaloids, such as (−)-sparteine and (+)-lupanine, are found in several plants of the subfamily Faboideae including the genus Lupinus. These molecules are characterized by a common chiral bispidine core [1] and possess a variety of biological activities, (−)-sparteine has both antiarrhythmic [2,3] and anticonvulsant properties and (+)-lupanine is moderately toxic [4]. Our group have been developing methods for the sustainable isolation of these alkaloids [5]. Currently, our research interests include using methodologies for the functionalization of bisquinolizidine alkaloids for medicinal chemistry applications. In this work, we present two synthetic strategies: a) synthesis of 17-substituted lupanine derivatives over the nucleophilic addition of Grignard reagents to the iminium ion derived from lupanine (Figure 1a); and b) synthesis of ammonium salts through *N*-alkylation reactions (Figure 1b). Finally, we present preliminary results of the biological activity of these bisquinolizidine derivatives.

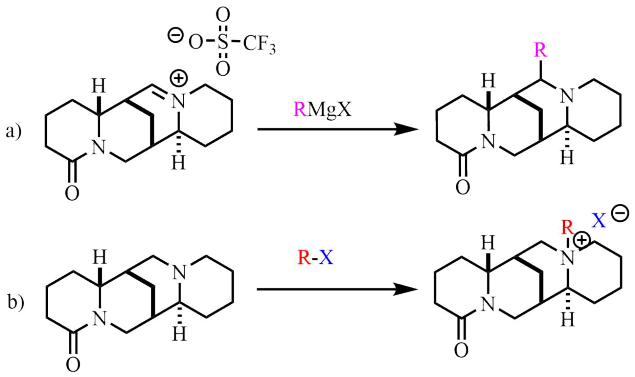

Figure 1. Reaction scheme of the addition of Grignard reagents (a) and alkylation reactions (b).

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P110

Silver(I) complexes containing different ligands as potent anti-cancer agents

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Cancer is considered one of the deadliest diseases nowadays and, despite advances in medicine, fighting it remains a challenge for society. In that frame, several silver compounds have been reported to possess promising anti-microbial and anticancer activity.[1]

Our research group developed a family of compounds with the general formula [Ag(L)(2,2'-substituted bipyridines)]$^{+}$ (L = phosphane) which revealed great potential for the treatment of resistant colorectal and ovarian cancers.[2] In order to continue the structure-activity studies and maximize the potential of the previously produced compounds, four new compounds were synthesized, namely [Ag(4,4'-dimethoxy-2,2'-bipyridine)(L)][CF_3SO_3] where L is triphenylphosphane (**1**), 1,2-bis(diphenylphosphino)ethane (**2**), (tris(4-fluorophenyl)phosphane) (**3**) or (tris(4-methoxyphenyl)phosphane) (**4**) (**Figure 1**). These compounds were characterized by NMR, UV-Visible, FT-IR and elemental analysis. Their cytotoxic activity will soon be tested in triple negative breast cancer cells (MDA-MB-231).

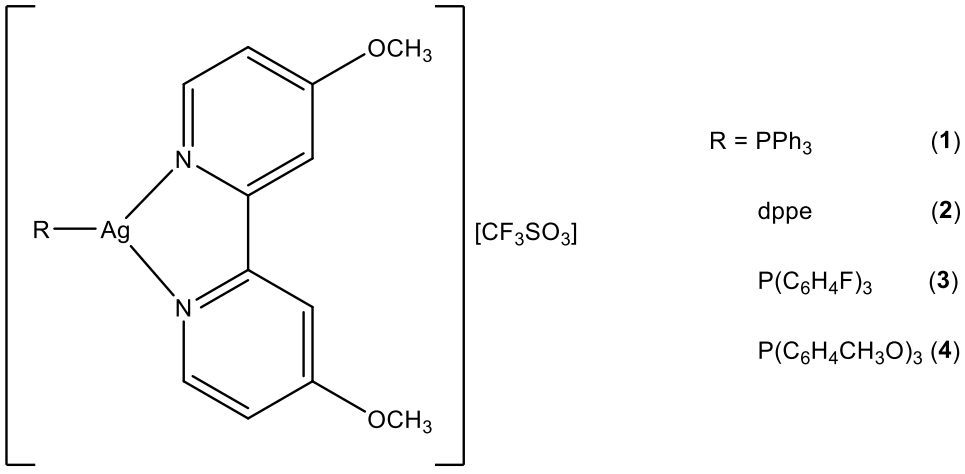

Figure 1. Chemical structures of compounds with general formula formula [Ag(4,4' OCH3 2,2' bipyridine)(L)][CF_3SO_3].

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. A.V. acknowledges the CEECIND 2017 Initiative (CEECIND/01974/2017).

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P111

Self-lubricating HEMA-based hydrogel with diclofenac eluting ability for therapeutic contact lenses

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When placed in the eye, contact lenses (CLs) disrupt the tear fluid, affecting the natural tribological equilibrium of the eye, as the contact mechanics between the tissues vary. This disruption can increase the contact pressure, resulting in frictional shear stress, ocular dryness and discomfort [1]. Therefore, continuous CLs wear can trigger inflammation. This is particularly critical for people suffering from dry eye. CLs surface modification to induce self-lubricating properties can be used to prevent or decrease the CLs related discomfort. The local action of anti-inflammatories may contribute to alleviate irritation symptoms. CLs may be advantageously used as platforms for the controlled release of these drugs [2].

In this work, hydroxyethylmethacrylate (HEMA) based hydrogels were loaded with an anti-inflammatory drug (diclofenac, DCF) and coated through plasma grafting with chitosan (CHI) and hyaluronic acid (HA). The potential of this system to be used in therapeutic CLs was evaluated. Material properties such as transmittance, wettability, ionic permeability and swelling were studied. Tensile tests and rheological tests were also carried out. Drug release experiments were performed with simulated tear fluid in sink conditions and under hydrodynamic conditions using a microfluidic cell that simulates the eye functioning. Chorioallantoic membrane (HET-CAM) tests were carried out to study potential ocular irritation. The variation of the coefficient of friction was analyzed using a nanotribometer. The samples were sterilized by high hydrostatic pressure (HHP).
The coating did not impair the studied physico-chemical properties, relevant for the application of the material in CLs. HET-CAM tests suggest that coated samples shall not induce ocular irritation. DCF release kinetics was controlled by the presence of the coating. As expected [3], the release rate was slower in hydrodynamic conditions than in sink conditions. The presence of the coating greatly reduce the coefficient of friction, improving the lubrication properties of the HEMA hydrogel surface. HHP has ensured sterilization without significantly changing the properties of the material, coating and drug.
In conclusion, the CHI/HA coating of the DCF loaded HEMA-based hydrogel is pointed out as an efficient strategy to obtain therapeutic CLs, without impairing relevant properties of the lenses for the intended application.

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P112

Computational evaluation of new isoniazide derivatives with antitubercular properties

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Tuberculosis (TB) is the infectious disease with the highest number of fatalities in the world and its treatment, in most cases, is still based on isoniazid (INH), one of the two most effective compounds in the fight against the disease. INH is still being used as a template for developing new compounds to fight TB. From a combination of experimental and computational studies three series of INH derivatives were developed and tested [1,2]. However, the most promising compound series, the alkyl hydrazide series (INH-aC_n), which presented excellent i*n silico* properties such as membrane permeability and spontaneous IN* radical formation, seemed to be too unstable in the aqueous medium, which impaired its antitubercular activity [2]. In this work, we aim to explore the role of halogenating the aliphatic derivatization in an attempt to slightly deactivate the C–N bond and provide the well-needed stability to this compound series. For that purpose, we systematically added halogen in different positions of the lipophilic tail of INH-aC_4 and estimated the IN* formation reactivity of the final derivatives using Quantum Mechanics calculations [2]. The fluorine and chlorine derivatives showed promising reactivities, quite similar to INH, while being expected to have a higher lipophilicity than the original compound. On the other hand, the bromine derivatives showed high reactivities, which would render them quite unstable. Overall, this study allowed us to have a larger understanding of the relation between halogenation and reactivity and may be key to developing new INH-based derivatives able to reduce the TB resistance problem.

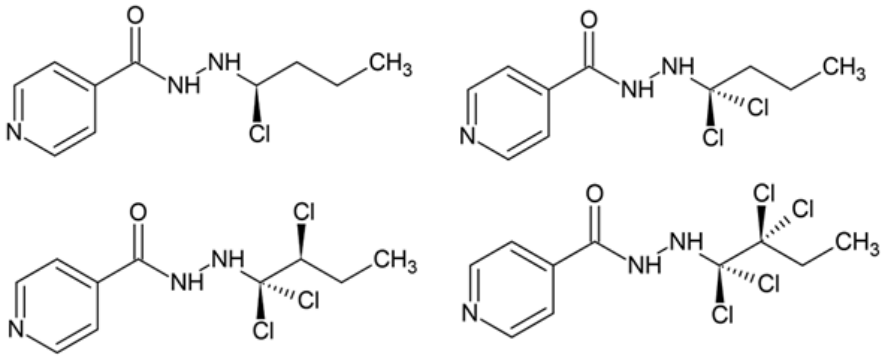

Figure 1. Examples of INH chlorine derivatives studied with our computational protocol.

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P113

Innovation Towards New Sugar-based Prodrug Scaffolds with Potential against Multidrug-Resistant Gram-negative Bacteria

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When it comes to the discovery and development of new antibiotics able to cope with antimicrobial resistance (AMR), Gram-negative bacteria are the WHO's top priority pathogens [1]. In addition to the inner membrane (IM) and the peptidoglycan (PG) cell wall, which are also present in Gram-positive bacteria, Gram-negative pathogens have a lipopolysaccharide (LPS)-containing outer membrane (OM) that significantly decreases their overall susceptibility to antibiotics [2]. Aiming to tackle this issue, this work takes the first steps towards the synthesis of new carbohydrate-based prodrugs with potential against multidrug-resistant Gram-negative bacteria. Inspired by the β-1,4 MurNAc-GlcNAc repeat unit of the PG as the natural substrate of PG glycosidases (PGG) [3], we have designed a prototype disaccharide exhibiting (**1**) a MurNAc analog for increased polarity and potential to enter the periplasm via OM porin channels; (**2**) a β-1,4 glycosidic bond to enable PGG-promoted hydrolysis in the periplasm; (**3**) a GlcNAc analog linked to a lipophilic dodecyl chain which, according to previous data [4], is expected to interact with the IM and lead to bacterial cell lysis. In this communication, the rationale behind the conception of these compounds (**Figure 1**) will be presented in detail, as well as the synthesis of the first disaccharide analogue of the series.

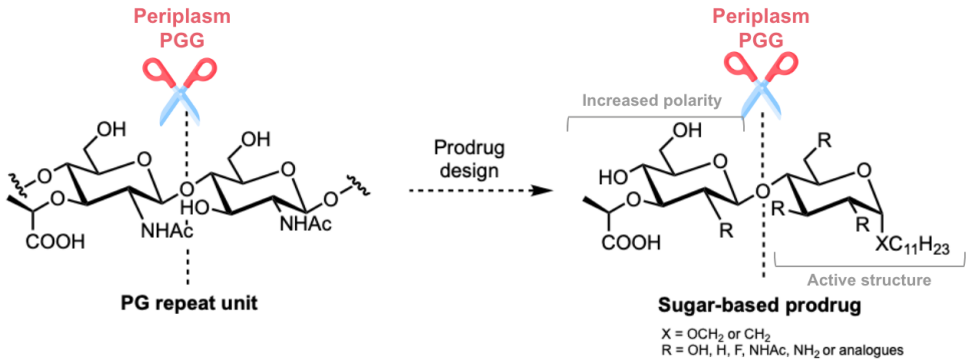

Figure 1. The rationale behind the synthesis of sugar-based prodrug disaccharides.

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P114

Early Detection of T cell Exhaustion by Microcalorimetry

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Immunotherapy is one of the most promising and innovative areas in cancer irradiation. About 50 % of cancer cases fail to be eliminated and often relapses. This phenomenon is, in general terms, corresponds to a dysfunctional response of these cells to immunological stimuli, losing their effectiveness [1]. The tumor has a high cellular metabolism and may thus drastically decrease the concentration of plasma glutamine. This glutamine depletion may reduce the proliferation of T-cells, impair the expression of surface activation proteins and the production of cytokines, which, for a prolonged period, contributes to the cellular exhaustion of T-cells, as they are auxotrophic for glutamine. Thus, the activation and exhaustion of T-cells will be monitored in a glutamine-poor medium [2]. This work aims to test microcalorimetry as an alternative method to flow cytometry for early detection of cell exhaustion. As a first step towards these aims, in fig.1 we show the effect of glutamine sub optimal levels in the proliferation of T-cells. Next step will include measurement of energy dissipation in the form of heat by microcalorimetry.

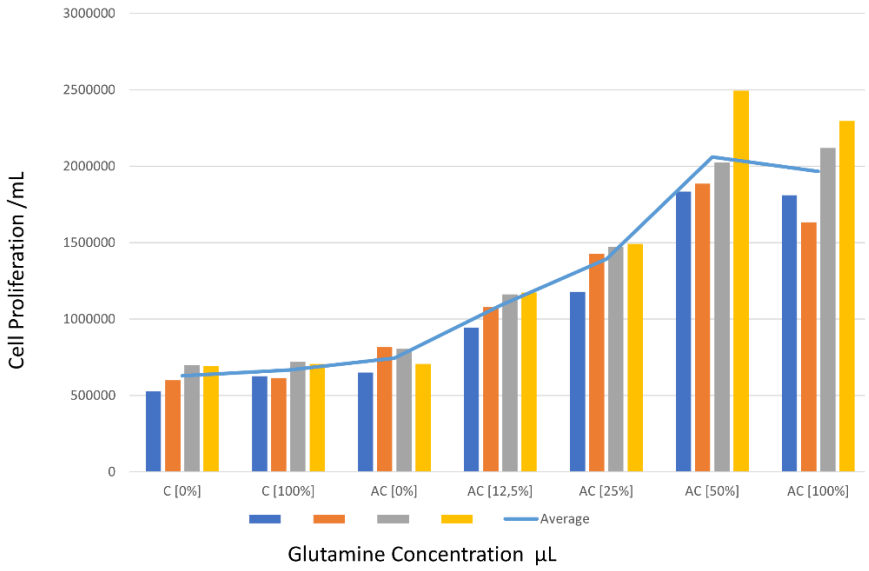

Figure 1. **T-cells proliferation for each glutamine concentration after 72 hours**. C represents controls and AC represents cells activated with CD3 and CD28 antibodies. An increase in the number of T-cells is observed according to the increase in glutamine concentration. Columns represent independent replicates.

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P115

Films and 3D printing pieces of photosensitive bioresin with active pharmaceutical ingredients

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Additive manufacturing is considered one of the most important emerging technologies in the last 10 years. Among the different 3D printing technologies available, stereolithography (SL) allows to print highly detailed pieces, in a layer-by-layer process resulting in advanced efficiency and lower production price [1,2]. The cured is provide by ultraviolet radiation which allows the production of biocompatible materials that cannot be exposed to high temperatures. New possibilities have been studied for devices and for the use of hybrid materials that combine biopolymers with active pharmaceutical ingredients (APIs) [3]. The present study reports the potential use of a photosensitive bioresin, derived from soybean oil, as good candidate to produce films and 3D printed pieces, dopped with different APIs (10 - 1% initial resin basis). Nimesulide, ibuprofen and paracetamol were chosen as model pharmaceutical compounds. Films were cured at 405 nm and 3D pieces produced using the stereolithography technique. Hybrid materials were chemical and mechanical characterized, and the dissolution profiles were recorded in ethanol, for 72h, spectrophotometrically.

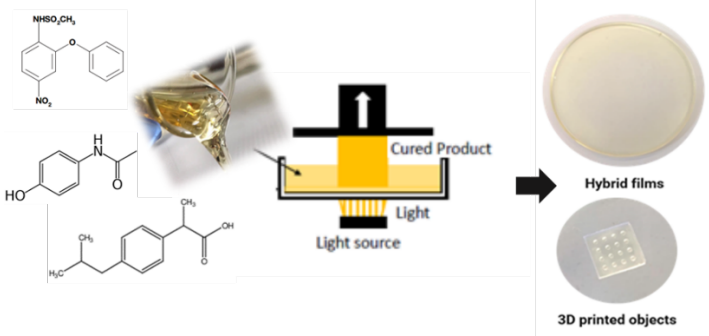

Figure 1. Films and 3D pieces of dopped bioresins manufacture by SL technique.

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P116

Exploitation in the synthesis of novel nucleosides based on a *N*-propargyl glucofuranuronamide template

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Over the last years the synthesis of new nucleosides and analogs has gained growing interest in the field of medicinal chemistry, being able to greatly fulfill demanding roles from antibacterial agents to anticancer or antiviral medication [1,2]. The research work presented in this communication was motivated by previous studies from our group that showed potent anticancer activities of *N*-dodecyl-containing glucuronamide nucleosides [3,4]. It aims to synthesize novel glucuronamide-based compounds based on furanose systems and comprising different nucleobases and a *N*-propargyl group (Figure 1) for further evaluation of their antiproliferative and antibacterial activities. For their synthesis D-glucofuranurono-6,3-lactone was used as precursor and it was converted into a suitable *N*-propargyl 1,2-di-*O*-acetyl glucuronoamidyl donor for further *N*-glycosydation with a silylated pyrimidine or purine derivative.

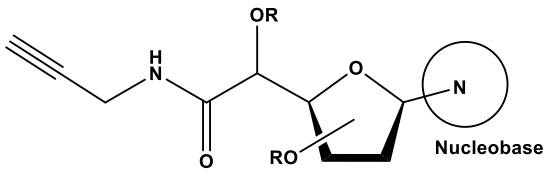

Figure 1 - General Structure of the Synthesized Nucleosides

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. The authors also thank FCT for financial support through grant CEECIND/03881/2018, exploratory project EXPL/MED-QUI/1017/2021

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Promotion of the anticancer / antibacterial activities of HAp composites through incorporation of Ag camphorimine complexes

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Coordination compounds are very attractive as biologically active molecules because they can combine anticancer and antimicrobial activities. Focused on the design of compounds that combine both types of activities, several complexes based on camphor derived ligands were synthesized and their anticancer and antimicrobial properties assessed [1-4]. Among them, silver-based complexes were selected to get an insight into the preparation of hydroxyapatite (HAp) composites and evaluation of their biological activity. HAp was chosen because it is a calcium phosphate widely used in bone reconstruction due to its biocompatibility and high osteo-conductive and osteo-inductive properties. Putting together in composites, the regenerative properties of HAp and the beneficial anticancer-antibacterial activities of the Ag(I) camphor imine complexes we expect to be able to reduce bacteria proliferation upon surgical bone reconstruction.

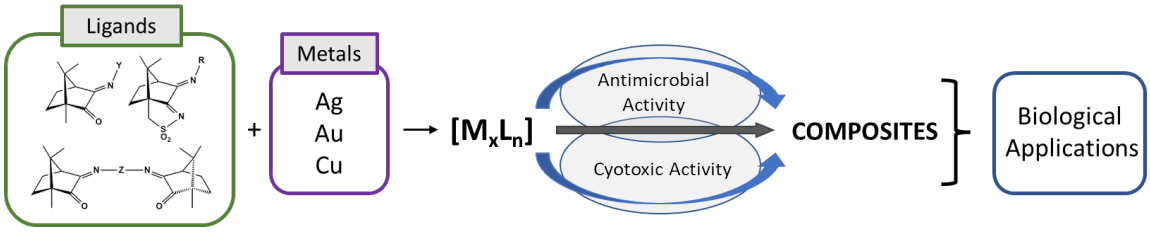

Figure 1. Synthesis of different complexes, selection of the ones with best activity for composites.

The overall aim of the work is the functionalization of biocompatible, bioresorbable and/or biodegradable materials with antibacterial and/or cytotoxic camphor derived complexes. The preliminary results show that the selected Ag(I) complexes have antimicrobial activity and high anticancer activity towards osteosarcoma cells HOS which is not lost in the composites.

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P118

Ruthenium-antibiotic conjugates as new potential dual-action therapeutic agents

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Despite advances in cancer treatment, mortality rates remain high, with millions of new cases and deaths reported each year worldwide. Current treatments, namely cisplatin, and its analogues have significant side effects and are often associated with drug resistance. These problems have stimulated a rising interest in the search and development of complexes of other metals with the aim of improving pharmacological properties. Over the years, our research group has been developing new Ru(II)(η^5-C_5H_5) complexes, some of which have exhibited higher cytotoxicity than cisplatin *in vitro* as well as antimetastatic activity *in vivo* against various types of cancer[1,2].

In 2018, 13% of all cancer cases diagnosed globally (excluding non-melanoma skin cancer were attributable to infections. Although these are mainly caused by viruses, data show that bacterially induced host cell manipulation can promote cancer formation [3,4]. Furthermore, infections caused by lower immunity are among the gravest threat to patients being treated for cancer, with multiple studies finding infection to be one of the leading causes of death in patients with a wide array of malignancies [5]. Aiming at developing a more efficient therapeutic approach, herein we conjugated a Ru(II)(η^5-C_5H_5) complex to different antibiotics, to obtain synergistic effects between them and/or modulate the anticancer/antibiotic properties. Thus, we report the synthesis and characterization (NMR, FT-IR, UV-visible spectroscopies) and biological evaluation of two new ruthenium-antibiotic conjugates that can potentially be used as a multifunctional anticancer agent. Their stability in aqueous/organic solutions was determined over time by UV-vis spectroscopy. These conjugates contain a linker sensitive to tumor microenvironment for controlled release of each component (cytotoxic complex/antibiotic), therefore their stability in aqueous solution at different pH values is also discussed.

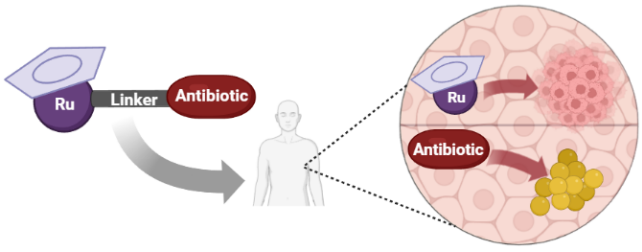

Figure 1. Multifunctional ruthenium-antibiotic conjugates.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This work was funded by FCT through project PTDC/QUI-QIN/0146/2020. T. S. Morais and J. A. S. Coelho thank FCT, as well as POPH and FSE-European Social Fund for Scientific Employment Stimulus Initiative for the projects CEECIND/00630/2017 (T.S.M.), 2022/00028/CEECIND (T.S.M.) and 2020/02383/CEECIND (J.A.S.C.).

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P119

Development of Green Approaches for Preconcentration of Local Anesthetics in Biological Matrices

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Local anesthetics like lidocaine, procaine, benzocaine and tetracaine (Figure 1) are commonly used in medical and dental treatments [1]. However, they can be used as cocaine adulterants [2] or as substances of abuse and may present toxicity to the central nervous and cardiovascular systems [1,3]. In this sense, it is necessary to develop analytical methods that allow, in a rapid and effective way, to monitor these analytes in complex biological matrices, while considering the principles of Green Analytical Chemistry.

In the present contribution, two green and innovative analytical techniques, *i.e.* bar adsorptive microextraction (BAμE) and solid phase microextraction LC Tips, were developed, compared and used for the preconcentration of four target anesthetics in biological matrices followed by gas chromatography coupled to mass spectrometry operating in the selected ion monitoring mode acquisition (GC-MS(SIM)) analysis. The procedure consists of several analytical steps, including extraction and back-extraction stages. Several parameters such as, extraction time, temperature, matrix pH, as well as back-extraction solvent type, time and liquid desorption mechanism, were optimized using specific design of experiments approach.

The preliminary results shows that BAμE devices have better efficiencies than LC Tips under similar optimized conditions. Both BAμE/GC-MS(SIM) and LC Tips/GC-MS(SIM) methodologies seem to be promising analytical alternatives to monitor these local anesthetics, given its great simplicity, easy handling and low cost.

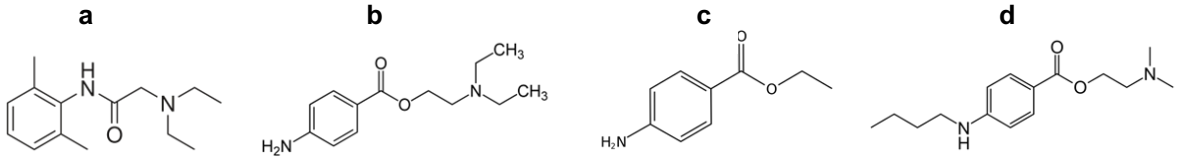

Figure 1. Chemical structures of lidocaine (a), procaine (b), benzocaine (c) and tetracaine (d).

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P120

Hybrid nanomaterials for enzyme-triggered release

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From a medical standpoint, the ideal disease treatment procedure would combine the diagnose and precise treatment at the same time, without delays between both processes and avoiding surgeries or drugs side effects. Nanoparticles are exceptional platforms for these functions. Because they can be traceable, target specific regions, be loaded with cargo and release it on-demand.[1]

The most used cancer treatment is conventional chemotherapy, however most of the administrated drugs have undesired side effects, short shelf life, limited bioavailability and uncontrollable biodistribution. Nanocarriers have emerged as the best solution for these problems. Their ability to protect the drug from biological interaction and to deliver it at the desired location might prove efficient in reducing the drugs side effects and increase their efficacy. Hybrid nanoparticles are qualified for controlled delivery applications, providing a simple and effective platform. By having an inorganic core combine with a polymeric shell it is possible to have biocompatibility, high drug loading and a controlled release mechanism. Fluorescent silica nanoparticles (SNPs) with a polymer shell of poly (D, L-lactide-co-glycolide) (PLGA) can deliver the anticancer drug doxorubicin, protect the cargo and releasing it intracellularly, while being traced.[2]

In this work, our objective is to increase the loading capacity of the hybrid SNP@PLGA nanocarriers by tunning the size of the PLGA shell. SNPs was synthesized by the Stöber method and labelled with a fluorescent perylenediimide dye. The surface of the SNPs was functionalized with (3-Glycidyloxypropyl)trimethoxysilane (GOPTS) and the epoxide ring was opened to produce hydroxyl groups. These hydroxyl groups were used as initiators in the ring opening polymerization of lactic acid (LA) and glycolic acid (GA) monomers, to prepare PLGA shells with different thickness. We expect to obtain new hybrid nanocarrier with improve load capacity to increase the performance of the control release nanoparticles.

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P121

Cyclam-based Mo(0) complexes as new antitumoral agents

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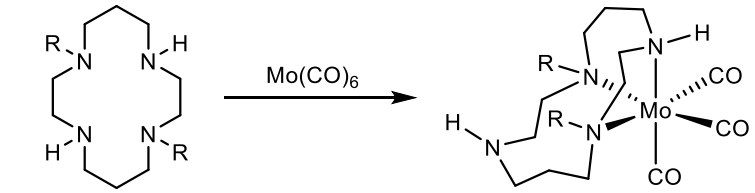
Cyclams are macrocyclic polyamines whose medical interest was fueled by the clinical trials of a bicyclam derivative for the treatment of AIDS [1] and for stem cell mobilization [2]. Recent studies have revealed that cyclams and their metal complexes display important antibacterial [3-5], antifungal [5] and antitumoral [6] properties. In this communication, we will present and discuss the synthesis, characterization and antitumoral properties of a new family of cyclam-based molybdenum carbonyl complexes.



R = H **1**
R = $^{4\text{-}CF_3}PHCH_2$ **2**
R = $^{3,5\text{-}Me}PHCH_2$ **3**

R = H **4**
R = $^{4\text{-}CF_3}PHCH_2$ **5**
R = $^{3,5\text{-}Me}PHCH_2$ **6**

Figure 1. Synthetic route for the preparation of complexes **4**-**6**.

Cyclam-based Mo(0) complexes of formulae [(H_2R_2Cyclam)Mo(CO)$_3$] (R = H, **4**, $^{4\text{-}CF_3}PHCH_2$, **5**, and $^{3,5\text{-}Me}PHCH_2$, **6**) were prepared in high yields by reaction of Mo(CO)$_6$ with H_2R_2Cyclam as depicted in Figure 1. The cytotoxic effect of all compounds was examined on human breast cancer cell lines (MCF-7 and MDA-MB-231) and reveals strong anticancer activity. Remarkably, [(H_2($^{4\text{-}CF_3}PHCH_2$)$_2$Cyclam)Mo(CO)$_3$] and [(H_2($^{3,5\text{-}Me}PHCH_2$)$_2$Cyclam)Mo(CO)$_3$] show a better performance than cisplatin in the conditions tested and, as far as we are aware, these compounds are the first molybdenum-cyclam complexes ever tested as antitumoral agents.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P122

Hybrid azole conjugates as viable anticancer and antimicrobial agents: a preliminary biological evaluation

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The need to develop new antibacterial agents that can circumvent the growing resistance of bacteria to antibiotics, along with exploration of revolutionary treatments for cancer are two demanding topics of the present times. Within this context, the present work discloses the synthesis and the antimicrobial and anticancer activities of novel molecules of structural basis saccharin–thiadiazolyl, saccharin–pyridyl and tetrazole–thiadiazolyl. Some of the compounds under study showed relevant inhibitory activity against Gram-positive (*S. aureus, S. epidermidis* and *M. smegmatis*), Gram-negative (*P. aeruginosa*) and yeasts (*S. cerevisiae* and *C. albicans*) strains. Besides, the compound *2-methyl-5-((1-phenyl-1H-tetrazol-5-yl)thio)-1,3,4-thiadiazole* (**TT**) exhibited a stimulating antiproliferative activity against human colon adenocarcinoma (HCT116), human breast adenocarcinoma (MCF-7) and melanoma (A375) cells, with GI_{50} values varying from 3.55 to 11.5 μM, in the same order of magnitude of those shown by Etoposide. Treatment of brain-like glioblastoma cells (U87) with **TT**, at the concentration of 100 μg/mL, induced a decrease on cells viability by 50% after 48 and 72 h. The cytotoxic potential of **TT** was also evaluated using glioblastoma (A172) and neuroglioma (H4) cell lines. Results attained for A172 cells have shown that **TT** only induces a significant decrease on cell viability upon treatment at 100 μg/mL for 72 h. A divergent observation was documented for H4 cells, where the treatment with such conjugate had promoted a significant decrease on cell viability (< 40-60%), even at concentrations as low as 0.39 μg/mL, after 24 h. Our results reveal the potential of hybrid azole-based conjugates, in particular the compound **TT**, as scaffolds worth further investigations, in the frame of antimicrobial and antineoplastic chemotherapy.[1]

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P123

Novel ruthenium-peptide conjugate for breast cancer targeted therapy

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Metastatic breast cancer (MBC) is a highly aggressive subtype of breast cancer that accounts for 15-20% of all breast cancer cases. Unfortunately, there is still no clinical cure for this subtype of cancer, and available treatments have limited effectiveness and often cause severe side effects due to their lack of specificity [1]. To overcome the limitations of existing therapies, our group is currently developing novel ruthenium smart metallodrug delivery systems capable of targeting both primary tumor and metastases of breast cancer [2]. These systems comprise a peptide that recognizes with high affinity the fibroblast growth factor receptor (FGFR), often overexpressed by MBC cells, linked to a cytotoxic ruthenium-cyclopentadienyl complex through a pH-sensitive function that responds to the slightly acidic tumor microenvironment. These systems allow accumulation, site- and time-specific release of the active species into the tumor (Figure 1).

Herein, we report the synthesis, characterization, and biological evaluation of a new pH-responsive ruthenium-peptide conjugate (RuPC) intended to be used as a smart metallodrug delivery system for MBC therapy. The two cytotoxic units of these systems, with the general formula $[RuCp(PPh_3)(NN)][CF_3SO_3]$ (NN represents different new monofunctionalized bipyridine ligands), were synthesized and fully characterized for the first time. The drug release profile was evaluated in solution at pH values that mimic the tumor microenvironment and the bloodstream. The *in vitro* cytotoxicity of the conjugate and the free complex was evaluated in four human breast cancer cells lines with different levels of FGFR expression.

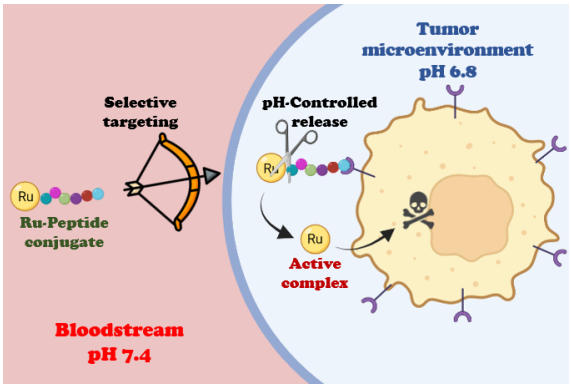

Figure 1. Proposed mechanism of action of the ruthenium-peptide conjugate.

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This work was funded by FCT through project PTDC/QUI-QIN/0146/2020. T.S. Morais and J.A.S. Coelho thank FCT, as well as POPH and FSE-European Social Fund for Scientific Employment Stimulus Initiative for the projects CEECIND/00630/2017 (T.S.M) 2022/00028/CEECIND (T.S.M) and 2020/02383/CEECIND (J.A.S.C).

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P124

Effect of surface functionalization of mesoporous silica nanoparticles on the dynamical behavior of encapsulated fenofibrate

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Fenofibrate (FNB) is a pro-drug which undergoes hydrolysis to the active fenofibric acid. It has been prescribed since the 1980's to treat hypercholesterolemia. To overcome its poor water solubility and improve its bioavailability, some of the recent formulations explore the incorporation in mesoporous silicas [1,2]. A correlation of the obtained results with the physical state of FNB was suggested, but not experimentally verified.

In this work we prepared spherical mesoporous silica nanoparticles (MSNs) with cylindrical pores of ~3 nm. Their surface was modified with either (3-aminopropyl)triethoxysilane (APTES) or trimethoxy(phenyl)silane (TMPS), in order to tune the hydrophilicity of the MSN pores, and ultimately the affinity with FMB.

Upon loading into the MSNs, FNB was amorphized in both unmodified and modified MSNs showing no tendency to undergo recrystallization in opposition to the bulk drug. Moreover, the onset of the glass transition, determined from calorimetric measurements, was shifted to lower temperatures when the drug was loaded in bare MSNs and in MSNs modified with APTES, while it increased in the case of incorporation in TMPS-modified MSNs. Changes observed in the dielectric response, both in the hydrated and the dried formulations, confirmed these differences and allowed us to disclose the broad glass transition in multiple relaxations associated with different FNB populations. Moreover, DRS showed relaxation processes in dehydrated composites associated with surface anchored FNB molecules, whose mobility shows a correlation with the observed drug release profiles.

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P125

Spotlight on the metal ion: Ru^{III}, Fe^{III} and Zn^{II} complexes supported by salen and salan ligands as anticancer agents

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Cancer has become a common public health concern, in our everyday lives, which derives from its concerning statistics: above 9 million deaths and over 19 million new cases, reported worldwide, in 2020 [1]. Chemotherapy based on platinum metallodrugs (cisplatin and its analogues) is still the most often used treatment, given their efficiency. Their debilitating side effects, limited activity range, acquired resistance and lack of efficiency towards metastasis have shown that the quest for effective and safe treatment remains an ongoing and urgent quest [2].

Metal complexes bearing alternative transition metals have been regarded as possible candidates. Ruthenium complexes have shown great potential, due to their anticancer properties (proven *in-vitro* and *in-vivo*) and the ability to overcome cisplatin's resistance [2]. Iron and zinc complexes are also promising anticancer agents, with good results regarding their cytotoxic properties, and have the benefit of having endogenous metal ions, that may present lower systemic toxicity, since the organism is better equipped to deal with them [3][4].

Equally important for biological performance are the ligands coordinating the metal ion and several studies have brought the focus on Schiff bases. These ligands provide numerous advantages, mainly due to their easy preparation, robustness, ability to coordinate almost any metal ion as well as therapeutic properties [5]. The *salen* and *salan* class of ligands are particularly interesting due to their (potential) tetradentate chelation mode, which imposes stability to the coordination compound [6]. Of the several families of compounds reported, in the context of metallodrug development, Fe(III) [3], Ru(II/III) [2] and Zn(II) [4] complexes supported by *salen* and *salan* ligands are still scarce and roughly unexplored.

In this work, we report the synthesis and characterization of new Fe(III), Ru(III) and Zn(II) complexes bearing *salen* and *salan* type ligands with the goal to evaluate both the impact of different metal ions and small changes in the ligand structure on the cytotoxic activity/selectivity, and on the overall biological response of the complexes.

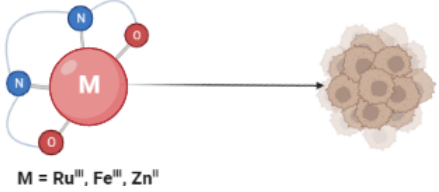

Figure 3 - Ru^{III}, Fe^{III} and Zn^{II} salen and salan complexes as anticancer agents [7]

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P126

Application of bar adsorptive microextraction (BAμE) to monitor trace levels of β-blockers in aqueous matrices

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β-blockers are a class of drugs that are among the most prescribed for the treatment of cardiovascular diseases and in other health situations, such as anxiety control. On the other hand, given the great effect they show in reducing tremors and blood pressure, these drugs have also been abused in several sports, with the World Anti-Doping Agency (WADA) banning their use [1,2]. Due to their high worldwide consumption and incomplete metabolization in the human body, β-blockers have been commonly detected in wastewater samples [3,4]. It therefore becomes important to develop alternative analytical methodologies to determine trace levels of β-blockers in biological and environmental matrices, in which passive microextraction techniques combined with chromatographic methods play an important role [1].

The present work aims to develop a new analytical methodology combining bar adsorptive microextraction with high performance liquid chromatography-diode array detection (BAμE/HPLC-DAD) to monitor trace levels of six β-blockers (atenolol, bisoprolol, carvedilol, nebivolol, pindolol and propranolol) in aqueous matrices [5]. The results obtained from different experimental conditions in the microextraction (type of sorbent phase, equilibration time, agitation speed, ionic strength, and pH) and back-extraxtion steps will be discussed. The application of the optimized and validated methodology to real matrices, i.e., urine and wastewater samples, is also addressed.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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Clinical Trials Assessing Nrf2 as Therapeutic Target

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The present systematic review aims to evaluate the clinical trials assessing Nrf2 as a therapeutic target. Being a major regulator of antioxidant enzymes and cytoprotective genes, Nrf2 has been studied as a therapeutic target in the treatment and prevention of several illnesses [1]. In our last research 62 clinical trials evaluating Nrf2 as a therapeutic target were registered in the following repositories: (1) clinialtrials.gov; (2) clinicaltrialsregister.eu; and (3) isrctn.com. In these trials, 25 evaluate drugs and 37 evaluate natural-occurring compounds, such as phytonutrients (curcumin, resveratrol, sulforaphane), peptides, hormones, and vitamins. Diseases under study include chronic (chronic kidney disease, chronic obstructive pulmonary disease), autoimmune (antiphospholipid syndrome, rheumatoid arthritis), neurodegenerative (Friedreich's ataxia, multiple sclerosis, Alzheimer's disease), cardiovascular (atherosclerosis, carotid stenosis) and cancers diseases (acute myeloid leukemia, lung, bladder, breast, and rectal cancer). Cancer is the most studied disease, with 16 trials evaluating drugs and 7 evaluating natural-occurring compounds. Natural-occurring compounds (37 trials) and drugs (12 trials) act as Nrf2 inducers, but some drugs (12 trials) can also act as inhibitors in the treatment of some cancers (Figure 1) that show constitutive activation of Nrf2 caused by mutations, which lead to tumour progression and metastases [2]. In conclusion, there is a reduced number of trials evaluating the activity of drugs on Nrf2 compared to the trials that have assessed the activity of phytonutrients and other components. In addition, Nrf2 inhibition in cancer treatment starts to gain relevance.

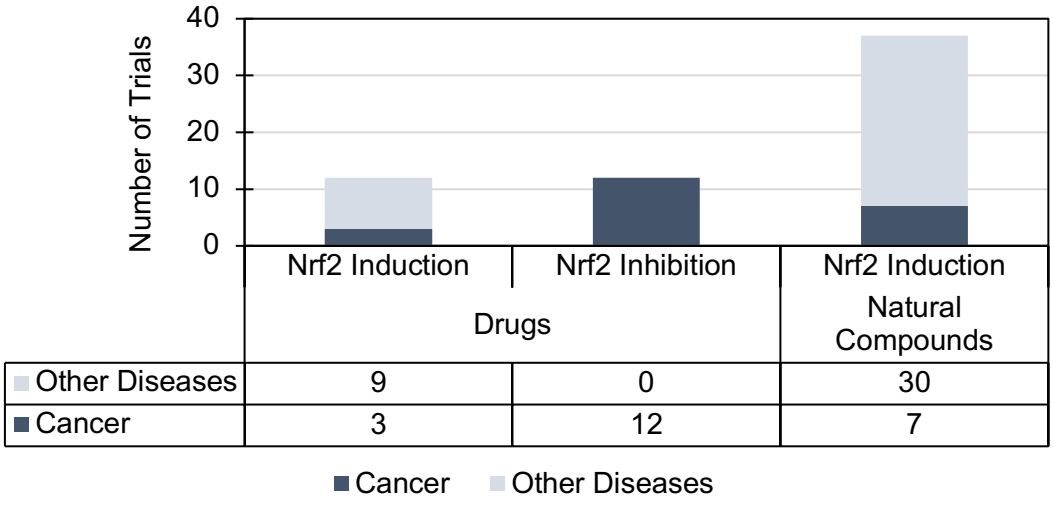

Figure 1. Number of trials that assess the therapeutic activity of drugs and natural-occurring compounds in Nrf2.

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Hybrid biopolymer films doped with bioactive coordination compounds: synthesis, characterization and antimicrobial activity

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Transmission of pathogens by infected high-touch surfaces is currently a major health concern that motivates the search for new strategies to prevent bacterial attachment [1,2]. This demand encourages the development of efficient antiseptic materials and coatings capable of reducing bacterial adhesion and biofilm formation [2].

In this context, this presentation will highlight the synthesis and characterization of new bioactive Ag(I), Cu(II), and Zn(II) coordination compounds (bioCCs) or coordination polymers (bioCPs), and the assessment of their antimicrobial activity after incorporation into hybrid biopolymer films. The coordination compounds were obtained by self-assembly method from simple metal salts and different benzoic acid building blocks, namely 4,4'-sulfonyldibenzoic acid, 4,4'-oxybis(benzoic acid), 4-(methylsulfonyl)benzoic acid, and 4-sulfobenzoic acid. All compounds were fully characterized by standard methods. Selected compounds were subsequently used in low amounts as active antimicrobial doping agents for two bio-based polymers, potato starch and agarose, resulting in the production of hybrid bioCPs- or bioCCs-doped biopolymer films (Figure 1).

Antibacterial activity of the obtained coordination compounds and derived hybrid materials was evaluated against Gram-positive (*S. epidermidis and S. aureus*) and Gram-negative (*P. aeruginosa and E. Coli*) bacteria. Bacterial biofilm development was likewise inhibited by the biopolymer films. The obtained results are encouraging, and further research toward the development of novel antimicrobial-doped hybrid polymer films is currently ongoing.

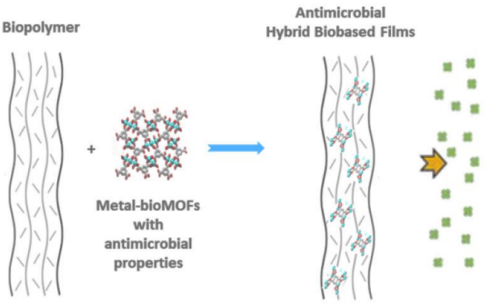

Figure 1. Schematic Representation of Assembly and Function of Antimicrobial Coatings.

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Exploring the effect of phosphane functionalization on 'RuCp' complexes: from synthesis to biological evaluation

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Acquired resistance against a variety of structurally unrelated anticancer drugs is one of the major obstacles in cancer treatment. In fact, the development of multidrug resistance (MDR) mechanisms is responsible for 90% of treatment failure in many forms of cancer. MDR involving the action of efflux pumps is one of the main mechanisms by which cancer cells develop resistance to traditional chemotherapy drugs, and the design of novel molecules capable to disturb (or inhibit) the normal functioning of these transporters is of upmost relevance. Over the last years, our research group has focused on the development of Ru(II)-cyclopentadienyl ('RuCp') metallodrugs with inhibitory ability for transporter pumps.[1,2] Recently, we disclosed the potential of a new family of 'RuCp'-derived compounds bearing 4,4'-R-2,2'-bipyridine ligands (with R = CH_3 or OCH_3) and PPh_3 as possible MDR chemotherapeutics, and some of them were found to be more cytotoxic against cisplatin-resistant than towards cisplatin-sensitive non-small lung cancer cells, which could be traced to their effect on cell efflux pumps.[2] Herein, we will follow our strategy to tackle MDR with Ru(II) compounds and explore the effect of varying the substituent at the aryl-diphenylphosphane moiety in a set of novel 'RuCp' complexes – $[Ru(Cp)(bipy)(PPh_2PhCOOR)][CF_3SO_3]$ (bipy = 2,2'-bipyridine derivatives, R= H, CH_2CH_2OH). Solution studies were performed on the $[Ru(Cp)(bipy)(PPh_2PhCOOH)]^+$ compounds using titrations followed by UV-Vis spectroscopy and based on the experimental data, all compounds were remarkably stable under the conditions used in the solution studies. We will also present our first results on the evaluation of their interaction with human serum albumin (HSA) by spectroscopic techniques to explore the eventual role of HSA in their biological behavior. The *in vitro* cytotoxicity of all compounds was measured against sensitive and multidrug resistant human colorectal cancer cell lines revealing, in some cases, activity in the low micromolar range which can disclose the new 'RuCp' as promising anticancer agents. Their antibacterial activity against *S. aureus* ATCC 25823 and *S. aureus* MRSA 43300 strains will also be discussed in this work.

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P130

Neurotoxic effects of Synthetic Cathinones: the potential role of metabolism

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Synthetic cathinones (Scat) constitute the first largest group of new psychoactive substances (NPS) seized in Europe, and are the second largest group in terms of the number of controlled substances[1]. The large number of emerging cathinones difficults the update of Scat's information by legal authorities and pose serious health risks[2]. The metabolic degradation of these substances adds one additional layer of difficulty for the legal/clinical control of these NPS. Nonetheless, metabolites can act as consumption biomarkers, extending the detection window beyond that allowed by the parent cathinone. Additionally, the metabolite profile can also shed some light into the mechanisms of toxicity, thereby opening avenues for the development of effective therapeutic options for the management of non-fatal intoxication cases and for understanding the molecular mechanisms of neurotoxicity induced by other toxicants.

We have recently reported the metabolic profile of a series of emergent Scat [3,4]. We have subsequently synthesized their major metabolites[5,6], which were then tested in differentiated human SH-SY5Y neuronal cell lines. All tested metabolites revealed to be more toxic than the parent cathinone. These preliminary results suggest that metabolism can have a key role in the onset of the adverse effects induced by this class of NPS.

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Synthetic cathinones used as drugs of abuse - bioavailability and biological effects

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In the last decade, an increased consumption of new psychoactive substances (NPS) as drugs of abuse has been globally identified. These substances are not part of the organizations' list of controlled substances. Furthermore, a wide range of NPS appeared driven by the introduction of small changes in the basic structure of the initial drugs, allowing these derivatives to circumvent legal restrictions.

NPS represent a threat to public health, not only because they mimic the effect of an illicit drug, but also as the impact associated to their consumption are still unknown, as several fatalities have already been related to these substances [1].

The 2nd most abundant class among NPS reported to EMCDDA (European Monitoring Centre for Drugs and Drug Addiction) are synthetic cathinones, structurally analogous to cathinone the main psychoactive alkaloid in Catha edulis plant [2]. Evidence indicates that the consumption of synthetic cathinones may be associated with several adverse effects such as agitation, dizziness, depression, hallucinations, and even death due to intoxication and/or liver damage. However, there is still lack of information regarding the understanding of these biological and toxicological effects.

This work aimed to increase knowledge about 8 synthetic cathinones which were already structurally characterized and seen to be hepato and neurotoxic. In this novel work we aim to evaluate the bioavailability of these 8 cathinone's using an intestinal cell line Caco-2 cell model of the gastrointestinal barrier, in order to evaluate its bioavailability, and further explore their cellular effect.

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Multifunctional hybrid polymer-silica nanoparticles for controlled release

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In recent years, hybrid nanoparticles have emerged as excellent candidates in chemotherapeutic delivery systems due to their functionalization versatility, biocompatibility and good colloidal stability, allowing targeting to tumour cells and controlled release of high local doses of therapeutic agents with low cytotoxicity to normal cells. Applications of silica nanoparticles (SNPs) has increased drastically due to the growing demand for new materials: through activation of surface, the chemical functionalization allows SNPs to be derivatized with a broad variety of functional groups, allowing the attachment of biomarkers, polymers, etc., to tune the interfacial properties of the nanoparticles.

In this communication, we present multifunctional fluorescent hybrid polymer-silica nanoparticles with a polymer shell of biocompatible poly(D,L-lactide-*co*-glycolide) (PLGA) and poly(N-acryloylmorpholine-co-N-acryloylsuccinimide) (pNAM-*co*-NAS) decorated with a tumor targeting agent (folic acid) [Fig.1]. First, the stability of the system is ensured by SNPs: it offers simple functionalization, adjustable size, good colloidal stability and biocompatibility. The nanostructure is synthesized to be optically traceable for a selective intercellularly accumulation. These points are achieved with the incorporation of a dye in the silica core, and folic acid, respectively. Moreover, assessing how p(NAM-*co*-NAS) behaves in the aqueous physiological environment, allows the evaluation of transport efficiency and contributes to the stability of the system, preventing aggregation in the biological media. The PLGA polymer is able to transport a hydrophobic cargo, the chemotherapy drug, Doxorubicin (DOX).[1] The hybrid nanosystem is expected to maintain its stability (even in the gastric environment) and loading capacity, from the time of administration until internalization into the tumor cells. Moreover, it is expected to interact selectively with the tumor cell, exploiting the interactions of folic acid with overexpressed receptors on the membrane. Within the cell, biodegradation of PLGA occurs through enzymatic pathways with the subsequent release and activation of DOX into the nucleus. The future prospective of this work is set on investigation of a drug delivery system that gives alternative routes of administration for DOX in chemotherapy treatments.

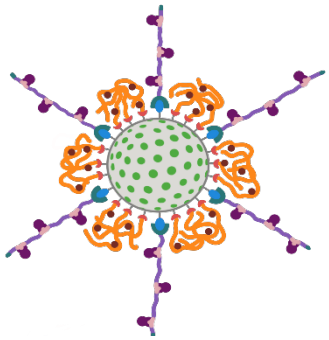

Figure 4 - Multifunctional hybrid polymer-silica nanoparticle. Fluorescent (green dots) SNP surface is grafted with PLGA (orange chains) for the enclosure of DOX (dark red dots) and with p(NAM-co-NAS) (purple and pink chain) covalently linked with folic acid (dark purple dots)

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Proteomics perspective application: Optimization of sample preparation for MS-based proteomics and metabolomics analysis

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Mass spectrometry is a very powerful analytical tool widely used for proteomics and metabolomics studies. These studies find application in medicine, as relevant pathological information can be extracted from the proteomic and metabolomics profile of diseased tissues. However, human samples are scarce and, when these come from hospitals, these tend to small and unique. Therefore, standardized and efficient sample preparation methods are required to make sure that all the relevant information can be retrieved from these samples.

The objective of this project is to optimize the experimental techniques for bottom-up proteomics analysis [1] for an array of tissues. In this work, pig tissue samples [2] from the myocardium, skeletal muscle and skin, were formalin-fixed and paraffin-embedded using the methodologies usually applied in hospital pathology laboratories, to emulate the preparation of biopsies for routine analysis. Then, several sample retrieval methods were applied, including retrieval protocols for formaldehyde tag removal. The processed tissues were then subjected to digestion and protein isolation techniques, followed by protease digestion and MS analysis.

Human serum samples were also employed to finetune the experimental preparation of samples for chemokine analysis. Different experimental approaches were tested for globulin depletion, and then samples were prepared following a classical bottom-up proteomics approach.

Data analysis is currently being performed to access which methodology for tissue processing better suits each tissue. From these data, a standardized protocol for sample processing will be developed and applied for human sample preparation of MS analysis. The final goal is to finetune the sample processing steps to improve MS-based clinical diagnostics.

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Nucleoside phosphate and phosphonate analogs as potential antibacterial agents

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Antibiotic resistance is a major global health concern and therefore the development of novel antibacterial candidates tackling this issue with innovative mechanisms of action are needed. Nucleoside and nucleotide analogs are important groups of molecules in medicinal chemistry, with various compounds approved as drugs, namely against cancer and viral infections [1]. Their potential application as antimicrobial agents has also been well reported in the literature [2,3], suggesting that nucleos(t)ide-like structures constitute promising scaffolds for the development of novel antibacterial agents. Besides being prompted to inhibit DNA synthesis, such molecules as well as structures mimicking partial frameworks contained in nucleotides, may also be able to inhibit bacterial cell wall biosynthesis by interfering in the pathways in which nucleotides and sugar phosphate biosynthetic precursors are involved. Therefore, various biological events and enzymes may be targeted by such structures, which enhances the opportunities for searching for alternative and unique mechanisms of action.

In this context, in this communication we report on the synthesis and antibacterial evaluation of a variety of triazole 5′-isonucleosides and nucleoside phosphonates constructed on xylofuranosyl templates. The triazole unit was envisaged as a potential neutral and rather stable surrogate of a phosphate group when combined with other moieties such as phosphonate or phosphate to establish new potential neutral diphosphate group mimetics. The synthetic methodologies used xylofuranose precursors and employed key steps such as sugar azidation, iodination, azide-alkyne 1,3-dipolar cycloaddition, phosphorylation, Arbuzov reaction or N-glycosylation.

Antibacterial assays revealed the therapeutic interest of some molecules, with compounds showing potent effects against the Gram-positive bacterial pathogen *Streptococcus pneumoniae*, including resistant strains, and with activities comparable or higher to those of a reference drug.

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Degradable Starch-Based Biopolymer Films Doped with Coordination Compounds for Antibacterial Applications

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This study describes the synthesis, characterization, and antibacterial characteristics of novel hybrid biopolymer materials doped with bioactive coordination polymers (bioCPs) and coordination complexes (bioCCs) [1-3]. Seven coordination compounds, $[Cu(NH_3)_2(nca)_2]$ (**1**), $[Cu(NH_3)_2(\mu\text{-ndca})]_n$ (**2**), $[Cu(NH_3)_2(\mu\text{-obba})]_n$ (**3**), $[Ag_4(\mu_8\text{-}H_2pma)_2]_n{\cdot}4nH_2O$ (**4**), $[Ag_5(\mu_6\text{-}H_{0.5}tma)_2(H_2O)_4]_n{\cdot}2nH_2O$ (**5**), $[Ag_2(\mu_6\text{-hfa})]_n$ (**6**), and $[Ag_2(\mu_4\text{-nda})(H_2O)_2]_n$ (**7**) were assembled from Cu or Ag sources ($Cu(NO_3)_2$, $AgNO_3$ or Ag_2O) and seven different building blocks: 2-naphthoic acid (Hnca), 2,6-naphthalenedicarboxylic acid (H_2ndca), 4,4′-oxybis(benzoic acid) (H_2obba), as well as pyromellitic (H_4pma), trimesic (H_3tma), homophthalic (H_2hfa), and 2,6-naphthalenedicarboxylic (H_2nda) acids. These compounds were used as active antimicrobial agents (dopants) in the development of doped biopolymer films, which were based on epoxidized soybean oil acrylate (ESOA), potato starch (PS), or its mixture with microcrystalline cellulose (PS-MCC). These model biopolymer materials can be adjusted to exhibit different rates of degradability/silver release. Both types of materials, coordination compounds and their hybrid biopolymer films with low bioCC or bioCP loadings (0.05-0.5 wt%), demonstrated remarkable antimicrobial activity against Gram-positive (*S. epidermidis* and *S. aureus*) and Gram-negative (*P. aeruginosa* and *E. Coli*) bacteria. The biopolymer films also inhibited the formation of bacterial biofilms (Figure 1). Overall, **1**-**3**@$[ESOA]_n$ revealed a particularly high performance against the clinical isolates of *S. epidermidis*; **4**@$[ESOA]_n$ outperformed other doped films in terms of antibacterial activity; **6**@$[PS]_n$ showed higher efficacy than **3**@$[ESOA]_n$, while **7**@$[ESOA]_n$ and **7**@$[PS]_n$ had similar antimicrobial and biofilm inhibition performance. This multidisciplinary study not only covers a wide range of relevant research topics, but it also broadens the antibacterial application of bioactive coordination polymers and hybrid biopolymer materials made from sustainable biofeedstocks such as soybean oil and potato starch.

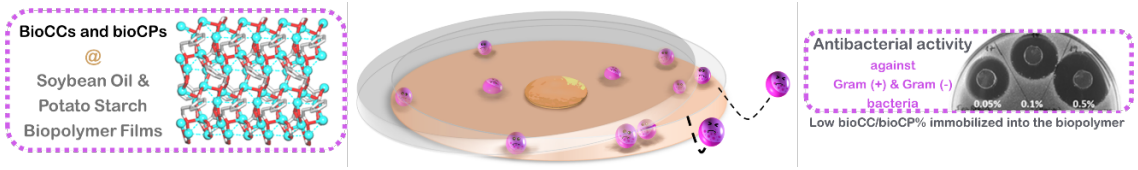

Figure 1.
Illustration of biofilm inhibition and antibacterial activity of hybrid biopolymer materials doped with bioactive coordination polymers.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This work was supported by the FCT and Portugal 2020 (projects PTDC/QUI-QIN/29697/2017, LA/P/0056/2020, IPL/2022/3DBioProd_ISEL, and REM2013), contracts under DL No. 57/2016, CEECIND/02725/2018, and CEECIND/00194/2020.
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P136

Sub-cloning and expression of recombinant human natural cytotoxicity receptors towards the development of a protein array methodology for ligand identification

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Natural cytotoxicity receptors (NCRs) are membrane proteins expressed by natural killer cells, part of the innate immune response. These receptors boost the immune system by assisting in the recognition and elimination of cancerous or virus-infected cells.

The main objective of this project is to subclone and express recombinant human natural cytotoxicity receptors (NCRs) to establish a novel and fast methodology for identifying potential activators for pharmacological applications.

A range of molecular biology techniques, including PCR, endonuclease, and cell transformation, were employed to subclone the *ncr1-4* genes and some of their natural ligands in *Escherichia coli* cells. The gens coding for NCR1, NCR3 and their natural ligand, NCR1 LG1 and NCR LG1, respectively, were successfully subcloned into expression ready pET vectors allowing for the routine production of these proteins. Conditions for protein expression, isolation and purification are currently being optimized in order to obtain sufficient amounts of these proteins in their native conformation.

Using protein immobilization techniques, polycarbonate plates will be functionalized with the purified receptors to build an array system that will be used in high throughput testing of chemical entities and ligands for NCRs. This system will contribute to the timely identification of molecules and/or fragments that can specifically bind to each receptor and prompt the development of new pharmacophores able to interact with NCRs and trigger or inhibit the activity of the immune system, leading to the development of innovative technologies in immunotherapy.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P137

Co-Crystallization as a Tool to Control the Solubility of Active Pharmaceutical Ingredients

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The low solubility of active pharmaceutical ingredients (APIs) is a major concern during the development of drug formulations, as it directly impacts the ability of a substance to enter the human bloodstream after ingestion. In the last decades, several strategies have emerged to address this issue, many of them relying on changes in the molecular organization of the drug in the solid state, leading to the establishment of a new field of research known as Crystal Engineering [1]. In this way, it is expected to control the intermolecular forces of the API in the crystal, which ultimately impacts its physical properties (e.g., solubility). Among the developed methodologies, co-crystallization (i.e., the preparation of crystalline solid materials in which the API is combined with other organic molecules) has become one of the most promising methodologies, as a judicious selection of a co-former allows the fine-tuning of the API physical properties. However, our current understanding of the formation of these materials is incipient, hampering our ability to produce these substances without resorting to expensive and time-consuming experimentation. This motivated the establishment of a research project in the Laboratory of Molecular Energetics (group 9) to systematically investigate the structural/energetic relations of co-crystal materials.

Nicotinamide (NIC) is a form of vitamin B_3 found in food and used as medicine due to its anti-inflammatory properties. Additionally, is often selected to produce co-crystals of other APIs due to its ability to form different types of hydrogen bonds. It is, therefore, an ideal candidate for systematic studies on the formation of this type of materials. Thus, the work here reported is part of ongoing research aiming the investigation of the co-crystallization of NIC with dicarboxylic acids (Figure 1), by evaluating how the solubility and the stability of the produced materials vary as the co-former is systematically changed in different stoichiometric quantities. The obtained materials were characterized by powder X-ray diffraction and differential scanning calorimetry, and their solubility was determined using an in-house made thermomicroscopy/light dispersion apparatus.

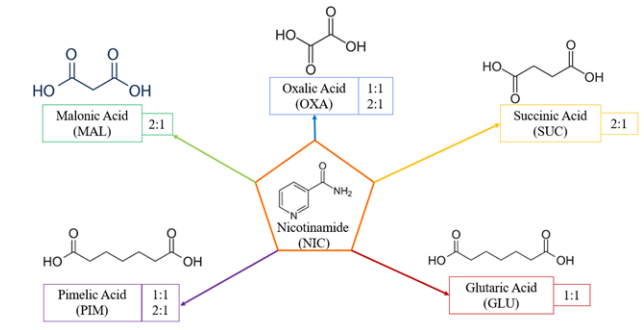

Figure 1. Scheme of the molecular structures of the API, the dicarboxylic acids and the defined stoichiometries of the co-crystals obtained for each co-former.

Acknowledgements: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P138

New fluorescent probes based on gallium(III) corrole complexes for the recognition of hydrogen sulfide: A journey from solution to intracellular site

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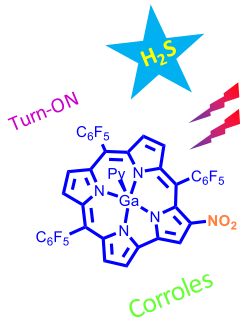
Hydrogen sulfide (H_2S) is a toxic gas with a foul-smelling, which has been recently recognized as an endogenous gaseous transmitter such as nitric oxide (NO) and carbon monoxide (CO). In the human body this gas, endogenously produced through enzymatic processes, performs essential biological functions, and is associated with various diseases. Unregular levels of H_2S are associated with Alzheimer´s disease, Down´s syndrome and diabetes [1]. Thus, from physiological and pathological point of view, it is important to develop sensitive and specific techniques for the detection of this gasotransmitter. Fluorescence imaging is the best technique for non-invasive in situ detection and mapping of H_2S in different media.

Corroles, the porphyrins analogues bearing a direct pyrrole-pyrrole linkage, are very promising as fluorescent chemosensors. Here we present fluorescent probes for detection of H_2S based on gallium(III) corrole complexes bearing nitro groups at β-pyrrolic positions. The response of the corroles to H_2S in solution and in intracellular medium is discussed [2]



Acknowledgments: Financial support is acknowledge from Fundação para a Ciência e Tecnologia (projects UIDB/00100/2020, UIDP/00100/2020,LA/P/0056/2020, PTDC/NAN-MAT/29317/2017, PTDC/QUI-QFI/29319/2017, LISBOA-01-0145-FEDER-029319, UIDB/50006/2020, UIDP/50006/2020, 2020.01763.CEECIND and REF.IST-ID/95/201) where applicable, co-financed by the FEDER and COMPETE2020, within the PT2020 Partnership Agreement.

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P139

Towards statin repurposing for cancer

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The research towards novel therapeutics in cancer treatment is arduous, time-consuming and expensive. To expedite drug development, in recent years, the off-target effects of approved drugs have been studied in repurposing studies.

Statins, a class of drugs widely used in the prevention of cardiovascular diseases, are also associated with several anti-cancer effects. In fact, a large number of clinical and epidemiological studies have described the anticancer properties of statins, but the evidence for anticancer effectiveness of statins is inconsistent. The lack of clear evidence, especially regarding the mechanisms by which statins exert their anticancer activity, is currently hampering their study as an adjuvant in cancer treatment.

In this work, we intend to unveil the effects that currently prescribed statins have in cancer models and extract information regarding their impact on regulatory pathways and cell death mechanisms.

In a first approach, different cancer cell lines will be treated with different statins such as lovastatin, rosuvastatin, simvastatin, pravastatin, cerivastatin, atorvastatin, and pitavastatin. These belong to two different classes of statins: type 1 (decalin) and type 2 (fluorphenyl). Cells exposed to these drugs will then be analyzed for their protein and metabolite content to identify changes to their regulatory pathways, using high-resolution mass spectrometry-based proteomics and metabolomics approaches. The differences relative to untreated controls will be grouped based on treatment type (statin type), dose and duration, allowing the construction of new correlation maps between statins / statin type and anticancer activity.

To evaluate the impact that the statin treatment on the viability of cancer cells, the viability of cells exposed to common chemotherapy drugs will also be accessed in the presence and absence of selected statins to better understand the possible synergistic effects that result in cancer cell death.

The ultimate goal of this work is to unveil the impact of statins in cancer cell biology by identifying their targets, correlate those targets with structural motifs in statins, and design a strategy to use statins in co-adjuvant therapies for cancer.

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P140

The primary cilia regulate the levels of thioredoxin reductase 1, γH2AX, and YAP in response to high glucose levels

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Diabetes is characterized by an abnormal ability to control the glucose level in the bloodstream, which can lead to other complications, such as hypertension, cardiovascular disease, and retinopathy. Dysregulation of glucose levels in the retina has been shown to increase hydrogen peroxide levels, leading to a disruption in the retinal blood barrier, one of the causes of diabetic retinopathy. The primary cilium is an organelle shown to play a role in controlling energy balance and glucose homeostasis. Defects in the structure and function of cilia can result in the development of various diseases, known as ciliopathies, which include overlapped phenotypes such as obesity and diabetes.

In this work, we intend to study the impact of increased glucose levels in primary cilia assembly in retinal pigment epithelium cell cultures (RPE-1). Also, we aim to understand the role of cilia in the cellular response to high glucose levels. For this, we supplemented the media growth of RPE-1 cells with different concentrations of glucose (5 mM, 25 mM, and 5 mM glucose + 20 mM mannitol). Then we induced cilia assembly before or after glucose supplementation. We observed that glucose supplementation did not affect the number of ciliated cells, but the cilia length was shorter in cells supplemented with 25 mM of glucose. To investigate the role of cilia in response to high levels of glucose, we evaluated the nuclear levels of (i) the thioredoxin reductase 1 (TXNRD1), one of the main enzymes involved in response to oxidative stress triggered by hyperglycemia; (ii) the γH2AX, a cellular marker of DNA breaks and cellular senescence; and (iii) the YAP, the effector of Hippo pathway signaling, that regulates fundamental biological processes, such as cell proliferation and apoptosis. We observed that adding glucose affects the nuclear levels of TXNRD1 and γH2AX, particularly at high levels (25 mM). Noteworthy, the presence of cilia, either before or after glucose supplementation, modulates the cell's response to high glucose levels. For example, in the case of YAP, its levels are altered in response to the glucose supplementation, and the presence of cilia affects this response, especially if their assembly occurs after the supplementation. These preliminary results show that the presence of primary cilia drastically affects the cellular response to high concentrations of glucose that are likely to induce oxidative stress and may play a crucial role in the development of diabetic retinopathy.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This work was funded by the Instituto Politécnico de Lisboa IPL/2021/ObeCil_ESTeSL and IPL/2022/WintCilGlu_ESTeSL

P141

Overcoming ß-lactam resistance in methicillin-resistant *Staphyloccocus aureus* - new molecular entities with the potential to fight MRSA

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Staphylococcus aureus is a major cause of hospital- and community-acquired infections worldwide, associated with a high mortality rate. Methicillin-resistant *Staphylococcus aureus* (MRSA) are isolates typically resistant to currently available antibiotics, in particular to β-lactam antibiotics, including penicillins, cephalosporins, and carbapenems. β-Lactam antibiotics target penicillin-binding proteins (PBPs), which are involved in the final steps of the bacterial cell wall assembly. However, MRSA strains express a protein (PBP2a) that can still catalyze cell wall biosynthesis in presence of β-lactams, allowing bacterial survival, and increasing virulence.

Previously developed work on the structure of PBP2a revealed the existence of an allosteric site responsible for the activity of the protein. Extensive computational studies have been performed within the research group yielding a set of possible scaffolds (Figure 1) able to block the allosteric site and prevent the activity of this enzyme.

Current work aims at defining a strategy for the synthesis of this family of compounds, resorting to organic synthesis techniques. The proposed structures contain a spiro motif as well as a fused lactam moiety, being these considered essential for the blocking of PBP2a's allosteric site.

The synthesized molecules will be tested for their ability to prevent MRSA growth. Their cytotoxicity on human cell lines will also be accessed in order to identify possible deleterious effects.

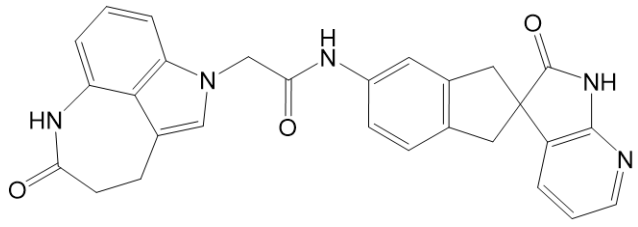

Figure 1. Structure of putative PBP2a allosteric inhibitors

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Smart Nanoparticles for Protein Controlled Delivery

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Over the last years, increase interest have been paid to drug delivery systems, given a special attention to mesoporous silica nanoparticles (MSNs) due to their high internal surface area and pore volume, tunable pore size, colloidal stability, and the possibility to selectively functionalize the internal (pores) or the external particle surface. This structural versatility has been the key element of the application of these nanoparticles in catalysis, corrosion, drug delivery, and biomedicine. [1-4]

Proteins are potent biotherapeutics that can be used in the treatment of several human diseases, for example cancer and diabetes. However, their low stability and large size pledge their therapeutic effects, and their delivery into the target place and in a controlled manner is still a challenge. [5]

In this study, 70 nm MSNs with 6 nm pore width were synthesized for the controlled delivery of lysozyme, through the different functionalization of the MSNs pores structure. To achieve this, MSNs were functionalized with two different molecules N-(trimethoxysilyl)propyl-N,N,N- trimethylammonium chloride (CAT) and trimethoxy(propyl)silane (PTES). We also use non functionalized MSNs (MSN-BARE) and Stöber nanoparticles as control materials. Our proof-of-concept system shows that the release kinetics depends on the functionalization of the particles, being faster for MSN-CAT than for MSN-PTES and MSN-BARE.

These results suggest that through different funcionalizations of this novel platform, it is possible to control the release kinetics of the cargo proteins.

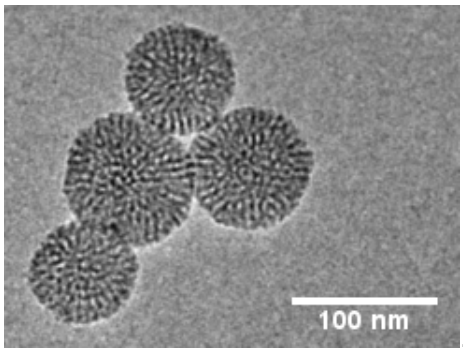

Figure 1. Large pore mesoporous silica nanoparticles; scale bar 100 nm.

Acknowledgments: Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e a Tecnologia through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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P143

New Analytical Approach for Cannabinoid Determination in Urine Samples

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Cannabis is the world's most widely used drug of abuse and most frequently associated with drug law offences in Europe, making it use an increase concern. *Cannabis sativa* L. is an annual herbaceous plant used for both therapeutic and recreational purposes. The main phytocannabinoids are synthesized and present in the plant in their acidic form, namely delta-9-tetrahydrocannabinolic acid, cannabidiolic acid, and cannabigerolic acid in which subsequently decarboxylated spontaneously in the plant or through heating (e.g. smoked), light exposure, oxidation, in the form of tetrahydrocannabinol (THC), cannabidiol (CBD) and cannabichromene (figure 1) [1, 2].

With the present work, we intended to develop and validate a new analytical approach for determination of 4 cannabinoids metabolites (CBD-OH, CBD-COOH, THC-OH, and THC-COOH) in urine samples, through bar adsorptive microextraction followed by microliquid desorption and gas chromatography coupled to mass spectrometry (BAμE-μLD/GC-MS) analysis [3].

The preliminary results shows that the proposed methodology obtained recovery up to 75% for the 4 targets compounds and seem to be promising analytical alternatives to monitor these cannabinoids, given its great simplicity, easy handling and low cost.

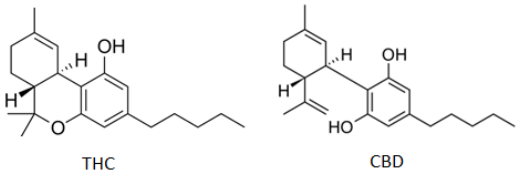

Figure 1. Chemical structures of THC and CBD.

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Bioinformatics & Multi-omics approaches to deep biological problems – sample processing for all!

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Untargeted omics approaches require complex samples containing the full *omes* of a biological system. Building on our expertise acquired at the Mass Spectrometry Facility at Técnico, we describe here a set of protocols that can be applied to various types of samples, including prokaryotic and eukaryotic cells, as well as animal and human tissue samples [1-3]. Following simple yet optimized extraction steps, samples are analyzed using different chromatographic conditions coupled to high-resolution mass spectrometry. Quantification of analytes, both at the metabolome and at the proteome level, allows identification of differences between samples to be performed without internal standards, using peak areas from total ion current for statistical analysis. Bioinformatics annotation of the results allows a pathway- and process-oriented analysis across biological sample conditions, prompting for a complete pathway interrogation.

The same bioinformatics approach can be applied to extensive studies in drug metabolism. In this framework, a complete protocol, aimed to elucidate the vast majority of possible *in vivo* drug transformation pathways, is shared, together with the required highlights for an adequate structural identification [1-3].

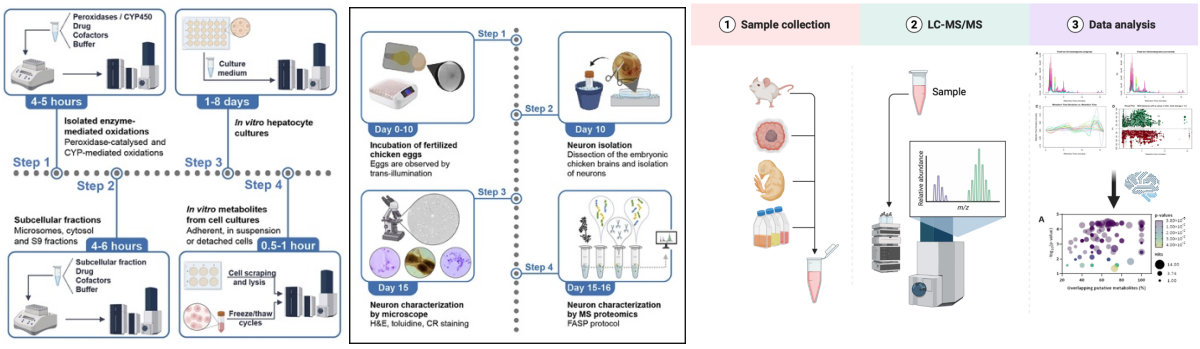

Figure 1. Bird's eye view of the global sample preparation protocols.

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