# CQE Days 2022

26th and 27th of May
Centro de Química Estrutural

Lisbon, Portugal

# BOOK OF ABSTRACTS

Plenary, Oral and Poster Communications

# CQE Days 2022

## Centro de Química Estrutural

26th and 27th of May
Lisbon, Portugal

## Book of Abstracts

**Edited by:** Amália Soares, Ana Cristino, Ana Marta de Matos, Ana Sofia Mestre, Ana Paula Carvalho, Carlos Bernardes, Ermelinda Maçôas, Gonçalo Justino, Isabel Correia, Jaime Coelho, Joaquim Marquês, Karina Shimizu, Nuno Neng and Tânia Morais

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# WELCOME MESSAGE

**Centro de Química Estrutural, from the Institute of Molecular Sciences**, is pleased to welcome you to the **4th edition of CQE Days**. The main purpose of the event is to share information about the research work carried out by researchers from CQE, through oral and panel communications (poster or poster + virtual pitch presentation to be shared on social media platforms), aligned with the four Thematic Lines of CQE:

- **SYNCat** - **Synthesis, Catalysis and Reactivity**, coordinated by Luísa Martins
- **MATSoft** - **Materials, Soft Matter and NanoChemistry**, coordinated by M. Fátima Montemor
- **SUSChem** - **Sustainable Chemistry for the Environment, Energy and Manufacturing**, coordinated by Isabel Marrucho
- **MEDLife** - **Medicinal and Biological Chemistry for Health**, coordinated by Matilde Marques

In addition to regular communications, the program includes plenary lectures from well-known invited researchers.

This year, CQE Days will return to a face-to-face format at **Faculdade de Ciências da Universidade de Lisboa**, where participants will be able to meet in person, share their work and discuss new ideas.

The Organising Committee wishes all participants a very fruitful meeting!

Lisbon, May 26th 2022,
The Organising Committee

# VENUE

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| **Registration C6** North Atrium
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| **Plenary Lectures and Oral Communications**: **C6** Auditorium 6.1.36
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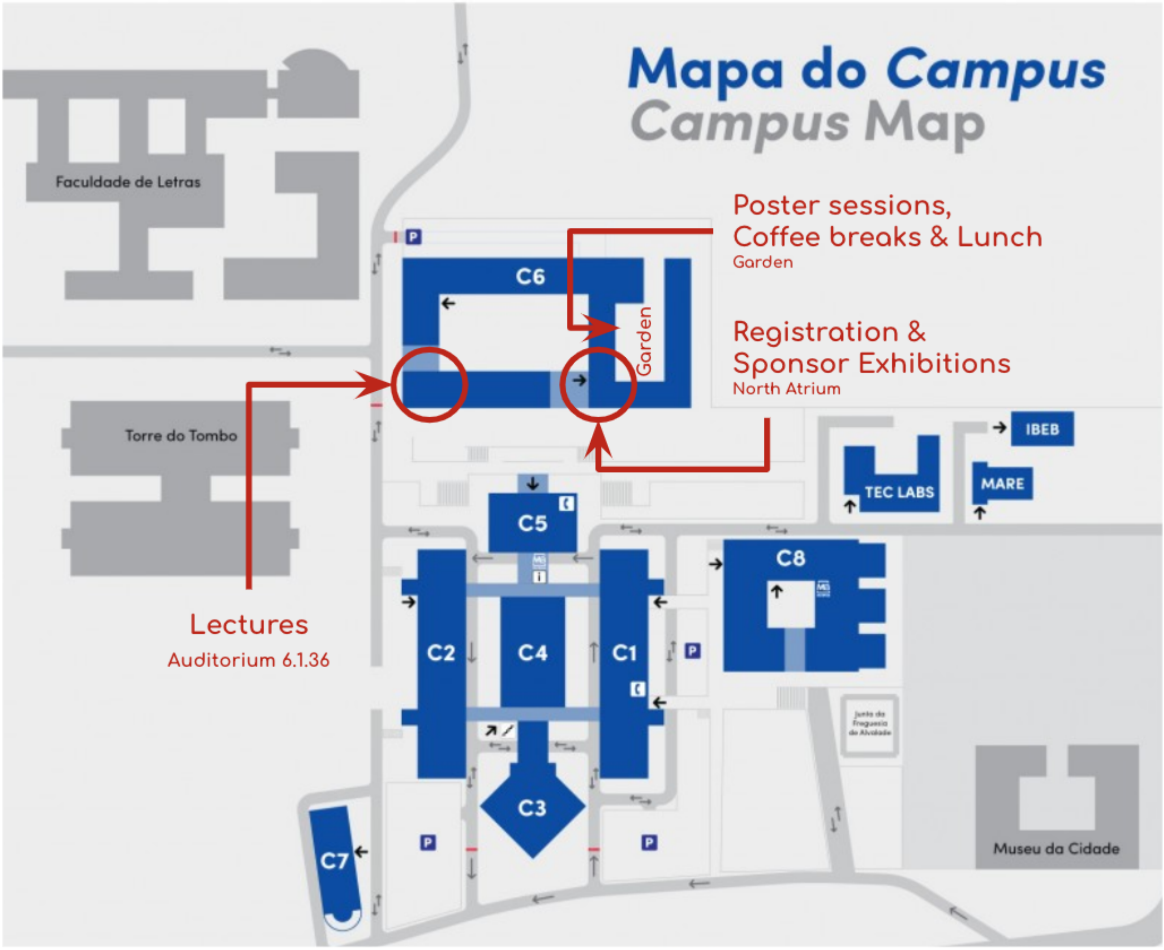
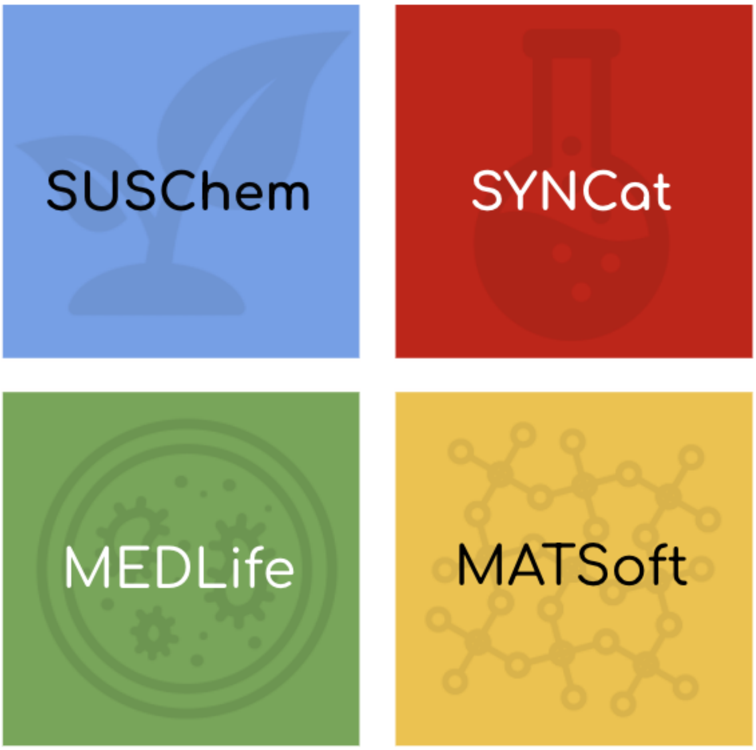
| **Poster Sessions**: **C6** Garden
| **Coffee Breaks**: **C6** Garden
| **Lunch**: **C6** Garden
| **Get together: C6** Garden



# CQE THEMATIC LINES

CQE has four thematic lines (TLs) which are aligned with the mission of the research centre. In this book of abstracts, each communication is linked with one or more TLs, that are identified using the following colour codes:



# PROGRAM

## Thursday, May 26th

| | |
|---|---|
| **8:30 - 9:00** | Registration |
| **9:00 - 9:30** | Opening Session |

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MATSoft

**Materials, Soft Matter and NanoChemistry**
Chairs: M. Fátima Montemor and Ermelinda Maçôas

| | |
|---|---|
| **9:30 - 10:15** | **PL1**<br>*Carbon dioxide utilisation technologies*<br>**Ana Machado** |
| **10:15 - 10:30** | **O1**<br>*Asymmetric poly(ionic liquid)-ionic liquid membranes for gas separation*<br>**Bruna Soares** |
| **10:30 - 10:45** | **O2**<br>*Directing surface functionalization of gold nanorods for improved optical biosensors*<br>**Pedro Paulo** |
| **10:45 - 11:45** | **COFFEE BREAK & POSTER SESSION** |
| **11:45 - 12:00** | **O3**<br>*Engineered biomass-derived activated carbons for water treatment*<br>**Marta Andrade** |
| **12:00 - 12:15** | **O4**<br>*Glutathione-Responsive Breakable Nanoparticles for Controlled Doxorubicin Release*<br>**Pedro Rosa** |
| **12:15 - 12:30** | **O5**<br>*Ag-based zeolites for climacteric fruit ripening mitigation*<br>**Ricardo Ferreira** |
| **12:30 - 14:00** | **LUNCH & POSTER SESSION** |

**14:00 - 14:20** **IMS Lecture: Rui Fausto**

**14:20 - 14:40** **IMS Lecture: António Silva**

SYNCat

**Synthesis, Catalysis and Reactivity**
Chairs: Luísa Martins and Ana M. Matos

**14:40 - 15:25** **PL2**
*The 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin macrocycle as a platform for heterogeneous catalysts*
**Mário Simões**

**15:25 - 16:10** **COFFEE BREAK & POSTER SESSION**

**16:10 - 16:25** **O6**
*$CO_2$ capture at medium temperature using MgO sorbents*
**Paula Teixeira**

**16:25 - 16:40** **O7**
*Hydrosilylative reduction of aldehydes and ketones catalyzed by a 2-iminopyrrolyl alkyl-manganese(II) catalyst*
**Tiago Cruz**

**16:40 - 16:55** **O8**
*Bimetallic Ni/Zeolite catalysts for $CO_2$ methanation: The influence of Cu and Fe incorporation*
**Daniela Spataru**

**16:55 - 17:10** **O9**
*Ion pair assisted tetrel bonds in heterometallic $\{Ni^{II}Sn^{II}\}\{Sn^{IV}\}$ and $\{Ni^{II}Sn^{II}\}\{Sn^{II}\}$ complex salts*
**Susanta Hazra**

**17:10 - 17:25** **O10**
*Adsorptive removal of organic dyes from wastewater using polyaromatic group containing Zn(II)-based coordination polymers*
**Anirban Karmakar**

## Friday, May 27th

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|---|---|
| **8:30 - 9:00** | Registration |

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**Medicinal and Biological Chemistry for Health**
Chairs: Helena Soares and Gonçalo Justino

| | |
|---|---|
| **9:00 - 9:15** | **O11**<br>*Cilia assembly affects thioredoxin reductase 1 translocation to the nucleus in response to increased glucose levels*<br>**Bruno Carmona** |
| **9:15 - 9:30** | **O12**<br>*From the lab bench to a clinical setting – CQE's Mass Spectrometry Lab in diagnosis*<br>**Gonçalo Justino** |
| **9:30 - 10:15** | **PL3**<br>*Designing functional materials using molecular recognition and mimetism*<br>**Cecília Roque** |
| **10:15 - 11:15** | **COFFEE BREAK & POSTER SESSION** |
| **11:15 - 11:30** | **O13**<br>*Gold nanorods decorated with glycoporphyrins for combined cancer photodynamic and photothermal therapies*<br>**Pedro Santos** |
| **11:30 - 11:45** | **O14**<br>*Hunting metastatic breast cancer with novel ruthenium smart metallodrug delivery systems*<br>**João Machado** |
| **11:45 - 12:00** | **O15**<br>*Conjugation of tetrapyrrolic macrocycles with graphene quantum dots: Application and future challenges*<br>**Carla Santos** |
| **12:00 - 13:30** | **LUNCH & POSTER SESSION** |

SUSChem

## Sustainable Chemistry for the Environment, Energy and Manufacturing

Chairs: Isabel Marrucho and Ana Cristino

| | |
|---|---|
| **14:00 - 14:45** | **PL4**<br>*Blue biorefinery contributing to a more sustainable environment and energy*<br>**Sónia Ventura** |
| **14:45 - 15:00** | **O16**<br>*Nanocatalyst-modified fibres for environmental remediation*<br>**Virgínia Ferreira** |
| **15:00 - 15:15** | **O17**<br>*Magnetically-responsive photonic pigments from nanoparticle self-assembly in batch*<br>**Tiago Martins** |
| **15:15 - 16:00** | **COFFEE BREAK & POSTER SESSION** |
| **16:00 - 16:15** | **O18**<br>*Metrological assessment of composition trends of oceanic areas by Monte Carlo simulation of georeferenced information – Application to characteristic oceanic parameters*<br>**Carlos Borges** |
| **16:15 - 16:30** | **O19**<br>*Solid-liquid-phase equilibrium: searching new systems for low temperature energy storage*<br>**Maria Sequeira** |
| **16:30 - 16:45** | **O20**<br>*Bar adsorptive microextraction (BAμE) applied to the determination of benzophenones in water matrices*<br>**Matilde Passos** |

| | |
|---|---|
| **16:45 - 17:00** | **AWARDS & CONCLUSIONS** |
| **17:00 - 18:00** | **GET TOGETHER** |

# Plenary Lectures

# PL1 Carbon dioxide utilisation technologies

Reis-Machado, A. S. [A*]; Messias, S.[A], Branco, L. C. [A]

A – LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
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Carbon Capture and Utilization technologies (CCU) are a key pillar towards a transition to a sustainable economy. The potential of these technologies for reducing $CO_2$ emissions was estimated to be 3.5 Gton-$CO_2$ eq in 2030 [1]. This talk will present several types of CCU technologies. Some of these processes are available now and contributing to reduce $CO_2$ emissions, other are at demonstration phase, while some other are being developed at laboratory scale. An overview of some CCU projects being implemented all over the world will be given. The climate community now recognizes the importance of CCU to move away from fossil resources. The key messages concerning CCU mentioned in the latest report of the Intergovernmental Panel on Climate Change (IPCC) [2] of the United Nations published in April this year will be highlighted. The importance of consistent life cycle analysis to ensure that developed processes will really benefit the environment will be illustrated.
This talk will be further focused on electrochemical reduction of $CO_2$. The significant progress that this technology has experienced in the last years will be analysed. This technology offers the attractive opportunity to produce fuels and chemical building blocks from $CO_2$, water and renewable energy. Key challenges at the level of electrode development, electrolyser design and testing of advanced electrolytes will be addressed describing in particular the work undertaken by the authors in this field [3].

**Acknowledgments:** This work was supported by the project "CO2RED – Understanding CO2 Electro-Reduction in Porous Materials" with reference PTDC/EQU-EPQ/2195/2021, funded by FCT – Fundação para a Ciência e Tecnologia. S. Messias is thankful to FCT for the fellowship SFRH/BD/147219/2019.

**References**: [1] A. Kätelhön, R. Meys, S. Deutz, S. Suh, A. Bardow; *PNAS*, **2019**, 116, 11187–11194. [2] IPCC, 2022: Summary for Policymakers. In: Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [P.R. Shukla, J. Skea, R. Slade, A. Al Khourdajie, R. van Diemen, D. McCollum, M. Pathak, S. Some, P. Vyas, R. Fradera, M. Belkacemi, A. Hasija, G. Lisboa, S. Luz, J. Malley, (eds.)]. Cambridge University Press, Cambridge, UK and New York, NY, USA. doi: 10.1017/9781009157926.001. [3] S. Messias, V. Paz, H. Cruz, C. M. Rangel, L. C. Branco, A.S. Reis Machado; *Energy Advances*, **2022**, 1, 277 - 286. DOI: 10.1039/D2YA00001F.

# PL2 The 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin macrocycle as a platform for heterogeneous catalysts

Mário M. Q. Simões[A*]

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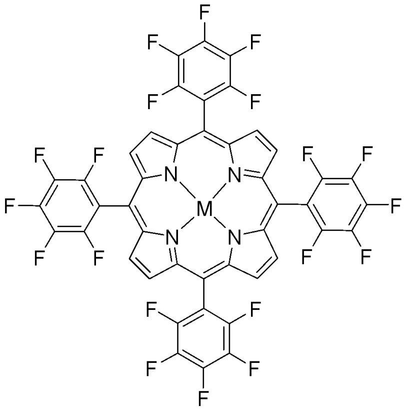
More than 25 years have passed since the publication of the first work carried out at the University of Aveiro concerning metalloporphyrins as catalysts in oxidation reactions [1]. Several students and projects have passed, leaving behind a significant collection of scientific papers, including reviews, but also master and PhD thesis, oral and poster communications and book chapters [2-6]. This communication intends to highlight the main achievements within the last few years, focusing on heterogeneous catalysis mainly.

The skeleton of the 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin free-base, $H_2(TF_5PP)$, besides the direct metalation into the corresponding metalloporphyrins, active homogeneous catalysts by their own, allowed us to develop a number of interesting chemical transformations on the macrocycle, which turned to be essential for several applications, including catalysis. Fluoride being the most reactive leaving group in nucleophilic aromatic substitutions, the presence of four fluorine atoms at the *o*- and *m*-positions of each $H_2(TF_5PP)$ aryl ring turns nucleophilic substitution of the *p*-fluorine atoms on those meso-aryl rings a useful and straightforward reaction in the presence of appropriate nucleophiles. Indeed, the combined electron-attracting effects of the four fluorine substituents allows the reaction to proceed so readily. Finally, the new macrocycles turned to be essential for the preparation of novel materials, which were studied as heterogeneous catalysts under different conditions.



**M = 2H; metal**

**Acknowledgements:** This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the project UIDB/50006/2020 | UIDP/50006/2020.

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# PL3 Designing functional materials using molecular recognition and mimetism

Roque, ACA[A,B*]

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Molecular recognition is ubiquitous in Nature and key for life, and it is on the basis of several scientific advances. In our group, we engineer molecular recognition events using biological and chemical tools to develop tunable materials with applications in bioengineering. In this context, the potential of affinity interactions to drive the design of affinity-triggered hydrogels for cell encapsulation and differentiation will be presented [1]. Furthermore, supramolecular assemblies can also be tuned to mimic the sense of smell and develop molecular recognition systems for analytes in the gas phase, which can be used in the context of clinical diagnostics [2,3].

**Acknowledgments:** This project has received funding from the European Research Council (ERC) under the EU Horizon 2020 research and innovation programme (grant agreement No. SCENT-ERC-2014-STG-639123, 2015-2022) and by the national funds from Fundação para a Ciência e Tecnologia, I.P. (FCT), in the scope of the project PTDC/BII-BIO/28878/2017, PTDC/CTM-CTM/3389/2021, UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences - UCIBIO and the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy - i4HB.

**References**: [1] Fernandes, C.S.M. et al. (**2020**) Natural Multimerization Rules the Performance of Affinity-Based Physical Hydrogels for Stem Cell Encapsulation and Differentiation. *Biomacromolecules* 21, 3081–3091. [2] Hussain, A. et al. (**2017**) Tunable gas sensing gels by cooperative assembly. *Adv. Funct. Mater.* 27, 1700803. [3] Palma, S.I.C.J. et al. (**2018**) Machine learning for the meta- analyses of microbial pathogens ’ volatile signatures. *Sci. Rep.* 8, 3360.

# PL4 Blue biorefinery contributing to a more sustainable environment and energy

Ventura, Sónia P.M

Departamento de Química – Instituto de Materiais de Aveiro, Universidade de Aveiro.
E-mail: spventura@ua.pt

Microalgae, macroalgae, and cyanobacteria are photosynthetic microorganisms, prokaryotic or eukaryotic, living in saline or freshwater environments. These have been recognized as a valuable carbon source, able to be used for food, feed, chemicals, and biopharmaceuticals. It is true that plenty of high-value compounds are being produced by these cells. As part of the set of bioactive compounds produced are the pigments, which include chlorophylls, carotenoids, and phycobiliproteins. Phycobiliproteins are photosynthetic light-harvesting and water-soluble. In this presentation the applications of these proteins as optical active centers and optical thermal sensors will be assessed [1,2]. Furthermore, a critical perspective on how harmful algal blooms management may be connected with biotechnology in the future. We have recently proposed the use of the biomass of cyanobacteria blooms physically removed in traditional control actions (much needed to ensure environmental and even human health safety) as a feedstock for future valorization, thus allying profit to water quality management, in a win-win relationship between economics and environmental sustainability [3].

**Acknowledgments:** This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, and Instituto de Telecomunicações, UIDB/50008/2020-UIDP/50008/2020, financed by national funds through the FCT/MEC (PIDDAC). The author acknowledges the financial support to FCT for the project REFINECYANO - Using biorefinery to value cyanobacteria pigments (PTDC/BTA-BTA/30914/2017).

**References**: [1] C. P. A. Carlos, S. F. H. Correia, M. Martins, O. A. Savchuk, J. A. P. Coutinho, P. S. André, J. B. Nieder, S. P. M. Ventura, R. A. S. Ferreira; *Green Chemistry* **2020**, 22, 4943-4951. [2] S. F. H. Correia, A. R. N. Bastos, M. Martins, I. P. E. Macário, T. Veloso, J. L. Pereira, J. A. P. Coutinho, S. P. M. Ventura, P. S. André, R. A.S. Ferreira; *Advanced Science* **2022**, 2104801. [3] I. P. E. Macário, S. P. M. Ventura, F. J. M. Gonçalves, M. A. Torres-Acosta, J. L. Pereira; *ACS Sustainable Chemistry & Engineering* **2021**, 9, 7182–7197

# Oral Communications

# O1 Asymmetric poly(ionic liquid)-ionic liquid membranes for gas separation

Soares, Bruna F.[A]; Marrucho, Isabel M.[A*]

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Non-solvent induced phase separation (NIPS) is one of the most used techniques to produce polymeric membranes from a wide variety of polymers. Nevertheless, this method has never been employed before in the preparation of poly(ionic liquid) (PIL)-based membranes [1-2]. The use of PILs and their derived materials incorporating ionic liquids (PIL−IL) has emerged as a highly promising strategy to design dense membranes with improved CO2 separation [3-4]. In this context, considering that membrane thickness is a critical parameter for their industrial scale application, this study is a step forward in the preparation of integral asymmetric PIL–IL membranes, with a top dense thin layer and a bottom porous layer. Solutions of poly([Pyr11][NTf2]) PIL and 20 wt% of [C4mpyr][NTf2] IL in acetone/dimethylformamide and acetone/formamide mixtures were prepared. The effect of several parameters of phase inversion process, namely, casting solution concentration and evaporation time, on the morphology (Figure 1) and gas separation performance of the resulting asymmetric PIL–20 IL NTf2 membranes, was evaluated and compared to those of dense PIL–20 IL NTf2 membrane. The results indicate that the choice of the appropriate solvent mixture strongly impacts membrane morphology and gas separation properties.

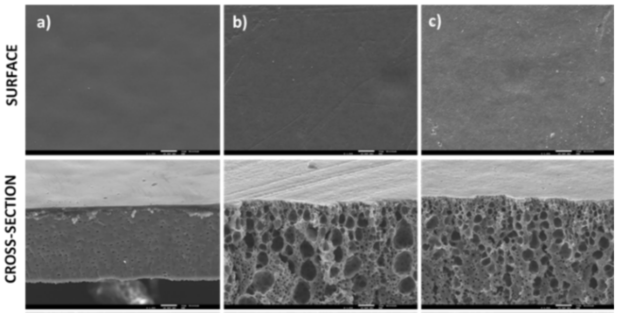

**Figure 1**. SEM images of PIL–20 IL NTf2/acetone: dimethylformamide membranes at solvent ratios of 80:20 and casting evaporation times of (a) 1, (b) 5 and (c) 10 min.

From SEM analysis, it was shown that the type of co-solvent used, dimethylformamide or formamide, as well as, different evaporation times strongly influenced the PIL–20 IL NTf2 membrane morphology. Regarding the CO2 permeances of the resulting asymmetric membranes a significant increase was observed. In particular, for PIL–20 IL NTf2/acetone: formamide (85:15) membrane a 10-fold increase in CO2 permeance was obtained compared with dense membranes, whereas only a small decrease in selectivity was observed.

**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. Bruna F. Soares gratefully acknowledges the financial support of FCT/MCTES (Portugal) for PhD fellowship 2021.05450.BD. This work was financed by CQE project (UIDB/00100/2020).

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# O2 Directing surface functionalization of gold nanorods for improved optical biosensors

Paulo, P. M. R.[A]*; Botequim, D.[A]; Oliveira-Silva, R. P.[B]; Serra, V. V.[A]; Viana, A. S.[A]; Zijlstra, P.[C]; Prazeres, D. M. F.[B]; Costa, S. M. B.[A]

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B – Institute for Bioengineering and Biosciences, Universidade de Lisboa.
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The strong interaction of gold nanoparticles with light, through the collective oscillations of free electrons in the metal, has been explored in many different ways to develop optical detection schemes for biochemical sensors. Generally, the detection scheme requires that target species interact with the particle's surface, which is typically accomplished by surface modification with specific molecular recognition units. The motivation behind the development of directed functionalization strategies, as opposed to indiscriminate surface functionalization, is based on a more rationale use of the nanoparticle's surface by directing the target species to its more sensitive regions (plasmon hot-spots) and leaving other surface regions available for different sensor functionalities, such as colloidal stabilization or anti-fouling coatings. In this contribution, we will discuss selected examples from our research of directed surface functionalization of gold nanorods for optical detection towards improved biosensors. The pursuit of such strategies has contributed to enhance single-molecule detection of proteins [1], and to the development of brighter fluorescent nanoprobes [2]. Recently, we have explored a new photoinduced plasmon-assisted strategy for targeting hot-spots in gold nanorods for surface functionalization with bioreceptor units [3]. The biotin-functionalized gold nanorods respond specifically to streptavidin binding, thus providing a model plasmonic biosensor with a total peak wavelength shift of ca. 4 nm (**Fig. 1**).

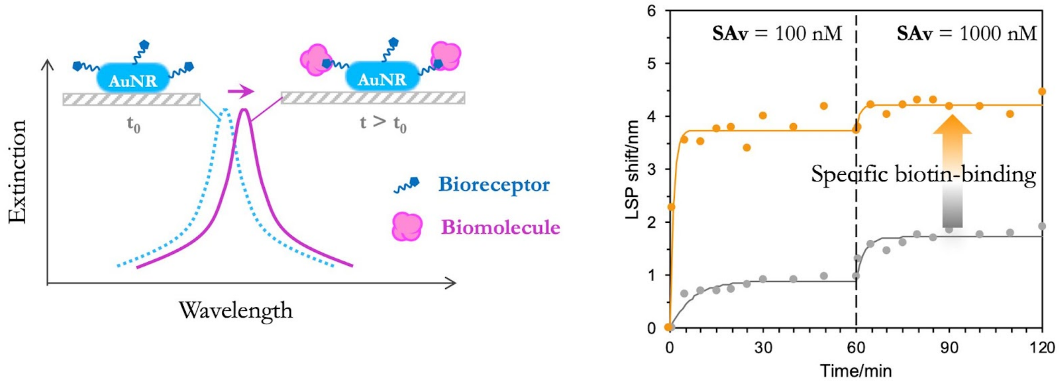

**Figure 1**. (left) Principle of optical sensing showing the plasmon peak shift upon biomolecule binding to gold nanorods (AuNR). (right) Plasmon peak shift (LSP) upon streptavidin (SAv) binding to biotin-AuNR (yellow) prepared by a photoinduced plasmon-assisted strategy.

**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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# O3 Engineered biomass-derived activated carbons for water treatment

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Water treatment improvement is mandatory to face current water quality challenges, being a focus of EU societal challenges and of CQE/FCUL and NES/LNEC strategic research. Activated carbon adsorption is considered one of the best available technologies to control the presence of pharmaceutical compounds (PhCs) in water [1]. The main objective of this work was the development of high-performing powdered activated carbons (PACs) prepared by steam activation of pine nut shells (PNS/Steam activated carbons) within the framework of EMPOWER+ project (Table 1). The developed PNS/steam (LP2, LP3) and good-performing commercial PACs (NSAES, NSAUF) were tested with primary ozonated water from Monte da Rocha drinking water treatment plant (in Alentejo, Portugal, with source water quality challenges). Assays were conducted with PAC fractions <20 μm particle size for the removal of three PhCs – diclofenac/DCF, carbamaze-pine/CBZ and sulfamethoxazole/SMX. These compounds were selected due to their recalcitrant behaviour during wastewater treatment and further persistence in the environment, including in drinking water sources [2]. The lab-made PNS/Steam PACs outperformed the commercial carbons in the kinetic assays for PhC removal from spiked water (Figure 1). These materials will be evaluated for different technologies/applications of PAC focused on drinking water treatment.

**Table 1.** Textural parameters, apparent density and $pH_{PZC}$ of PNS/Steam and commercial PACs.

| | $A_{BET}$ $m^2/g$ | $V_{total}{}^{a}$ $cm^3/g$ | $V_{meso}{}^{b}$ $cm^3/g$ | $V_{micro}{}^{c}$ $cm^3/g$ | App. density $kg/m^3$ | $pH_{PZC}$ |
|---|---|---|---|---|---|---|
| **LP2** | 1386 | 0.98 | 0.57 | 0.41 | 316 | 10.5 |
| **LP3** | 1192 | 0.74 | 0.38 | 0.36 | 386 | 10.1 |
| **NSAES** | 1103 | 0.71 | 0.30 | 0.41 | 349 | 9.1 |
| **NSAUF** | 1194 | 0.87 | 0.60 | 0.27 | 332 | 8.6 |

[a] Evaluated at p/p0 = 0.975 in the $N_2$ adsorption isotherms at −196 °C; [b] Vmeso – mesopore volume, difference between Vtotal and Vmicro (width between 2 and 50 nm); [c] $V_{micro}$ – total micropore volume (width lower than 2 nm).

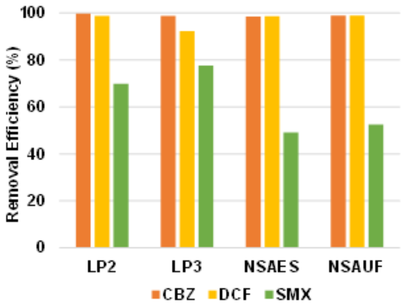

**Figure 1.** PhC removal efficiency by PNS/Steam and commercial PACs (100 μg/L each PhC, 10 mg/L PAC, 24 h contact time).

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# O4 Glutathione-responsive breakable nanoparticles for controlled doxorubicin release

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In recent years, the fields of nanomedicine and nanotechnology have grown at an unparalleled rate, and one of the main applications is the development of controlled drug delivery systems, with precise temporal, spatial and dosage control. Implementation of such systems requires the use of biocompatible hybrid materials with trigger-responsive capabilities to ensure that the drug is only delivered in the desired location. This precise control derives from the requirement to avoid side effects when administer drugs such doxorubicin (DOX) using conventional methods, due to the cytotoxicity to healthy cells.

Mesoporous silica nanoparticles (MSNs) are exciting materials due to their high internal surface area and pore volume, tunable pore size, colloidal stability, and the possibility to selectively functionalize the inner (related with 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. In the last years, significant progress has been made in controlling the characteristics of mesoporous silica materials, mainly the particle size and pore structure [1-3].

In this communication we present the preparation of glutathione-responsive MSNs by integrating disulfide bonds within the silica network. These nanoparticles are expected to respond to the higher concentrations of glutathione commonly present in tumor cells, causing the degradation of the silica nanoparticle and releasing of the cargo (DOX). We have performed release kinetics in simulated physiological conditions, and our proof-of-concept system showed that MSNs with incorporated disulfide bonds, had higher release kinetics as well as high retainability of DOX in non-triggering conditions. The system also showed the ability to withstand conditions similar to the human stomach, opening excellent prospects for oral administration approaches.

**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 authors acknowledge the financial support from Fundação para a Ciência e a Tecnologia (FCT), European Union (FEEI), QREN, FEDER (02/SAICT/2017) and COMPETE (PTDC/CTM-CTM/32444/2017 (02/SAICT/2017/032444), UIDB/00100/2020 and UIDP/00100/2020).

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# O5 Ag-based zeolites for climacteric fruit ripening mitigation

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The Food and Agriculture Organization (FAO) estimates that approximately 33% of all food produced worldwide is simply lost, with up to 45% of the total corresponding to fruits/vegetables [1]. Climacteric fruits present a postharvest ripening associated with some respiration gases and production of Volatile Organic Compounds (VOCs). The most important one is ethylene, a natural ripening hormone [2]. Ethylene removal can be achieved by adsorption process, a cheap method when compared with others. Zeolites present as a natural solution due to their characteristics of good sorbents, while also being suitable for stabilizing metal clusters (e.g. Ag) [3].
This work aims for the study of silver ZSM-5 zeolites for the efficient adsorption of ethylene. Ethylene breakthrough curves experiments were performed using a mixture of gases, $C_2H_4$ (50 ppm), He (10 % vol.) and $N_2$. Experiments were performed under dry or humid (80 % RH) conditions to see the effect of water presence. ZSM-5 with different compensation cations ($Na^+$ and $H^+$), different Si/Al ratios (15 and 40) and different amounts of Ag were used. Fig. 1a shows the effect of Ag and water on the sample's ethylene capacity. For NaZSM-5 sample (Si/Al=15) with no metal, ethylene capacity is very low. Introduction of Ag strongly enhances ethylene capacity. However, in presence of water, this later decreases substantially. In Fig. 1b, one can see that with increasing Ag amounts, ethylene adsorption capacities also increase, although many factors can contribute (Si/Al, compensating cation, nature and amount of Ag). TPR experiments and UV-Vis studies were performed to give insights on the nature of the different metal species. Indeed, results show that cationic metal species might be responsible for the increase in performance of these zeolite adsorbents.

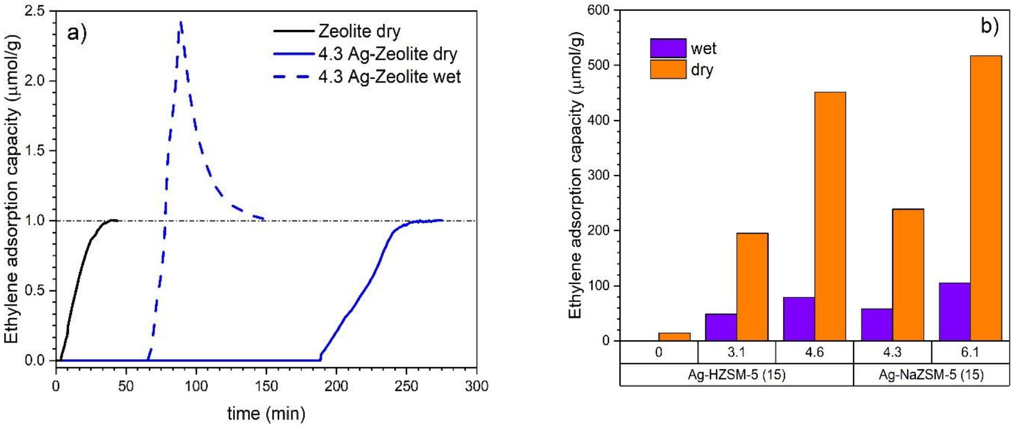

**Figure 1.** *a) Breakthrough curves* of NaZSM-5 zeolite with and without Ag, under wet and dry conditions; b) ethylene adsorption capacity of Ag-ZSM-5 zeolites (Si/Al=15; $Na^+$ or $H^+$) under wet and dry conditions.

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# O6 $CO_2$ capture at medium temperature using MgO sorbents

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MgO is a medium-temperature sorbent (200-400 ºC), that in terms of carbon capture and storage (CCS) has been investigated for both post and pre-combustion $CO_2$ capture technologies. After the $CO_2$ capture process, the carbonated MgO sorbent can be regenerated, and the concentrated $CO_2$ stream can be valued in downstream applications.

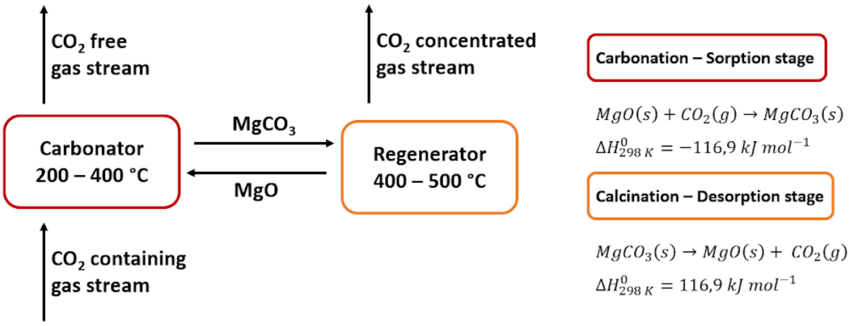

**Figure 1**. Cyclic $CO_2$ removal process based on MgO sorbents.

MgO presents a high theoretical $CO_2$ capture capacity (1.09 g of $CO_2$/ g of MgO), small regeneration energy, wide availability and low price. The highest drawback of MgO is its poor capture capacity coupled with slow kinetics. In this work, $CO_2$ capture capacity was enhanced by the synthesis of nanosized MgO using the sol-gel method. The sorbent performance was further improved by the addition of supports Ca and Ce-based, and by the doping with alkali metal salts (AMS), using molar percentages of 15 %, 25 % and 35 % of single salt $NaNO_3$ and of a mixture consisting of $NaNO_3$, $LiNO_3$ and $KNO_3$.

Cyclic stability was investigated by multiple carbonation/calcination cycles tests using a fixed-bed reactor. After 10 cycles under 100 % of $CO_2$ sorption atmosphere, Ca and Ce-based supported MgO sorbents impregnated with 15 % of ternary mixture registered carrying capacities of 100 mg $CO_2$/ g sorbent and 152 mg $CO_2$/ g sorbent, respectively, considerably higher than the 44 mg $CO_2$/ g sorbent achieved for the unsupported sorbent. The improved $CO_2$ carrying capacity of supported sorbents can be explained by the reduction of nitrates sintering and segregation, since their dispersion on the sorbent seems to be enhanced, and by the improvement of sorbent's properties along the carbonation/calcination cycles (e.g., higher stability of surface area). Textural, mineralogical and morphological characterization of the fresh and spent sorbents was made using XRD, $N_2$ sorption and SEM techniques, respectively.

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# O7 Hydrosilylative reduction of aldehydes and ketones catalyzed by a 2-iminopyrrolyl alkyl-manganese(II) catalyst

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The reduction of carbonyl groups is present in the synthesis of many commodity chemicals [1]. Metal-catalyzed hydrosilylation has become an important alternative for such reactions, owing to the stability and versatility of organosilicon compounds. However, to maximize the sustainability of those catalytic processes, there has been a shift towards earth-abundant-based catalysis. With manganese, the contributions concerning hydrosilylation have still been few [2]. Recent manganese-based catalyst systems were able to perform hydrosilylations at room temperature and below 1 mol% catalyst loads [3], but complete mechanistic discussions were absent.
Using our previous experience with the coordination chemistry of iron and cobalt with 5-substituted-2-iminopyrrolyl ligands and its applications in hydroboration [4], this work reports the synthesis and characterization of an alkyl-manganese(II) complex bearing a 5-aryl-2-iminopyrrolyl ligand **1** capable of catalyzing the atom-economical hydrosilylative reduction of aldehydes and ketones to the respective alcohols. Utilizing very mild conditions, a maximum turnover frequency of 95 min$^{-1}$ was obtained, via a silyl-Mn(II) mechanistic route, as asserted by a combination of experimental and theoretical efforts [5].

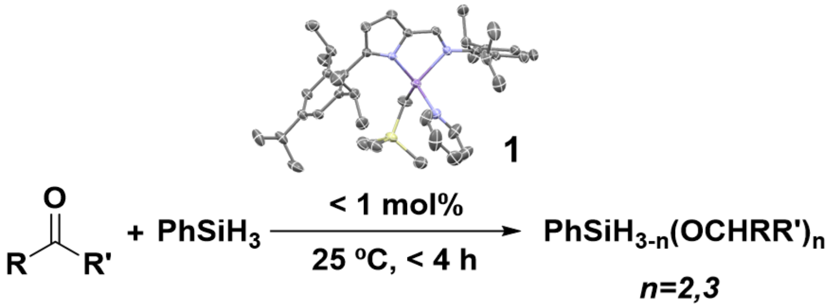

**Figure 1**. Hydrosilylative reduction of aldehydes and ketones catalysed by **1**.

**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. We thank Fundação para a Ciência e a Tecnologia for the financial support (Projects UID/QUI/00100/2019, UIDB/00100/2020, UIDP/00100/2020 and PTDC/QUI-QIN/31585/2017).

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# O8 Bimetallic Ni/Zeolite catalysts for $CO_2$ methanation: The influence of Cu and Fe incorporation

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Nowadays, reducing greenhouse gases (GHG) emissions is mandatory in order to reach the ambitious goal of zero net emissions, i.e., climate-neutrality by 2050. $CO_2$ conversion into synthetic fuels, integrated with renewable energy pathways and efficient catalytic systems, became both a challenge and an opportunity to decarbonize several industrial (e.g., cement) and energy sectors. Indeed, $CO_2$ hydrogenation using green hydrogen, produced via water electrolysis with renewable energy (Power-to-Gas), is one of the most promising $CO_2$ utilization routes. More specifically, the hydrogenation to $CH_4$, which is a clean energy vector with high calorific value, is considered an effective solution to store the excess of renewable electricity in the natural gas grid, and it reveals high potential for the future towards a circular economy and low carbon society [1] [2].

$CO_2$ methanation requires the use of catalysts due to the stability of $CO_2$ molecules. Thus, transition (e.g., Ni, Co, Cu, Fe) and noble (e.g., Ru, Rh) active metals have been used, while several metal oxides and micro/mesoporous materials have been considered as supports. Ni catalysts present more interesting properties in terms of cost-efficiency, but their low resistance towards deactivation requires the use of promoters [3]. As an alternative to rare-earth metal oxides (e.g., $CeO_2$, $La_2O_3$), incorporating a secondary transition metal such as Fe or Cu could result in suitable interactions able to promote the catalytic performances.

In this study, bimetallic $Ni_{15}M_1$/USY zeolite (M = Fe, Cu) catalysts were synthesized by co-impregnation (15 wt% Ni, 1 wt% Fe/Cu), characterized, and tested under $CO_2$ methanation conditions, with the aim of identifying the potential promoter effect of Fe and Cu. For comparison purposes, monometallic $Fe_{15}$/USY, $Cu_{15}$/USY and $Ni_{15}$/USY catalysts were also studied. While the incorporation of Cu led to weaker Ni-support interactions and no beneficial effects on $Ni^0$ dispersion, Fe induced stronger interactions responsible for the formation of smaller and better dispersed $Ni^0$ particles. Consequently, the incorporation of Fe was accountable for a remarkable enhancement of the catalytic performances, both in terms of $CO_2$ conversion and $CH_4$ selectivity (~72% and ~100%, respectively; 325 ºC, 5 bar, 86 100 mL $h^{-1}$ $g^{-1}$).

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# O9 Ion pair assisted tetrel bonds in heterometallic $\{Ni^{II}Sn^{II}\}\{Sn^{IV}\}$ and $\{Ni^{II}Sn^{II}\}\{Sn^{II}\}$ complex salts

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Crystal structure and theoretical calculations on the ion pairs of two types of heterometallic $\{Ni^{II}Sn^{II}\}\{Sn^{IV}\}$ (type **I**) and $\{Ni^{II}Sn^{II}\}\{Sn^{II}\}$ (type **II**) complex salts (Figure 1) synthesized from the self-assembly reaction of the salen type Schiff base $H_2L^1$, $H_2L^2$ or $H_2L^3$ with the adequate mixture of $NiCl_2{\cdot}6H_2O$, $SnCl_2$ and $SnCl_4{\cdot}5H_2O$ are presented [1]. Ion pairs in the crystal structures of these obtained salts interact *via* a variety of $M^{II}{\cdots}Cl$ interactions (M = Ni, Cu or Sn) along with H-bonds. Detailed geometrical analysis reveals that $Sn^{II}{\cdots}Cl$ interactions are dependent on the oxidation state of the metal halide donor, being lengthened with the higher oxidation state ($Sn^{II}$ to $Sn^{IV}$). Structural comparison with the $\{Cu^{II}Sn^{II}\}\{Sn^{II}\}$ derivatives of $H_2L^1$ and $H_2L^2$, reveals that the length of other $M^{II}{\cdots}Cl$ interactions ($M^{II}$ = Ni or Cu), being dependent on the halide acceptor [$Ni^{II}$ ($d^8$) or $Cu^{II}$ ($d^9$) system], decreases from the $d^8$ metal ion system to the $d^9$ one. The nature of ion-pair interactions was further investigated by DFT calculations with application of the QTAIM, ESP, NBO and NCI methods. Significant charge transfer from the Cl to Sn atoms allows the characterization of the $Sn{\cdots}Cl$ interactions in these complex salts as an uncommon ion pair assisted $Sn{\cdots}Cl$ tetrel bond.

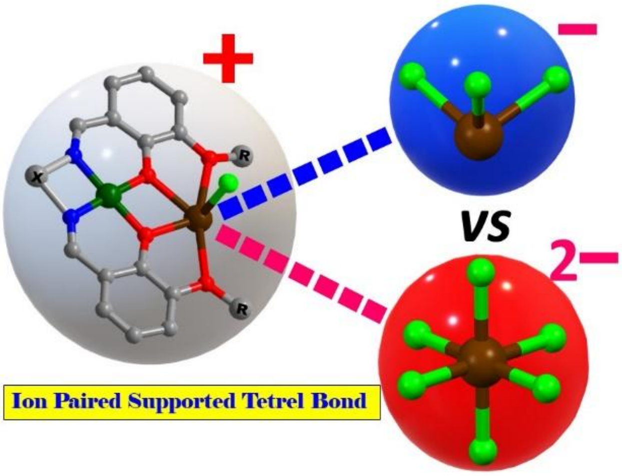

**Figure 1**. Ion pair assisted $Sn{\cdots}Cl$ tetrel bonds in heterometallic $\{Ni^{II}Sn^{II}\}\{Sn^{IV}\}$ (type **I**) and $\{Ni^{II}Sn^{II}\}\{Sn^{II}\}$ (type **II**) complex salts.

**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. S.H. expresses his gratitude to Instituto Superior Técnico and Fundação para a Ciência e a Tecnologia (FCT) for scientific employment contract (no.: IST-ID/103/2018) under Decree-Law no. 57/2016, of August 29.

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# O10 Adsorptive removal of organic dyes from wastewater using polyaromatic group containing Zn(II)-based coordination polymers

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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 Zn(II) coordination polymers (CPs), formulated as $[Zn(L1)(DMF)(H_2O)_2]_n.n(H_2O)$ (**1**), $[Zn_2(L1)_2(DMF)(CH_3OH)]_n$ (**2**), $[Zn(L2)(DMF)]_n$ (**3**) and $[Zn(L2)(4,4'\text{-Bipy})]_n$ (**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 zinc nitrate under solvothermal conditions. The synthesized CPs were used for the adsorption of various cationic and anionic organic dyes in aqueous medium, which was monitored by UV-Vis spectroscopy. Amongst all the coordination polymers, CP **1** bearing an anthracene group is the most effective one for the removal of different types of dyes (both cationic and anionic) with a removal efficiency of 96-99% [3]. The adsorption kinetic, adsorption isotherm and thermodynamic parameters of CP **1** were also determined. However, the pyrene tagged CPs **3** and **4** can selectively remove (removal efficiency of 97-98%) only the cationic methylene blue (MB) dye from an aqueous solution. The recyclability tests show that the CP **1** can be recycled at least three times without a marked decrease of its dye removal capacity.

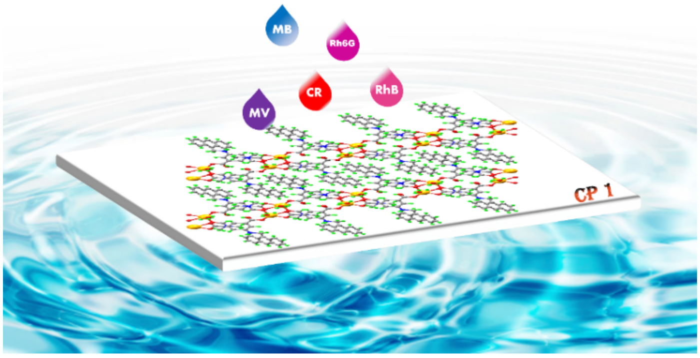

**Figure 1**. Adsorptive Removal of various cationic and anionic dyes using CP 1.

**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. A. Karmakar and A. Paul expresses their gratitude to IST and FCT for Scientific Employment contract (Contrato No: IST-ID/107/2018 and IST-ID/197/2019) under Decree-Law no. 57/2016, of August 29.

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# O11 Cilia assembly affects thioredoxin reductase 1 translocation to the nucleus in response to increased glucose levels

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Obesity is considered a major health issue caused by a metabolic imbalance and is associated with adverse consequences such as the development of cardiovascular disease, neurodegenerative disorders, and type 2 diabetes [1]. Diabetes is characterized by a reduced ability to control the level of glucose in the bloodstream leading to other complications, such as hypertension, cardiovascular diseases, nephropathy and retinopathy [2]. Dysregulation of glucose levels in the retina has been shown to increase $H_2O_2$ levels, leading to a disruption in the blood-retinal barrier, a hallmark of diabetic retinopathy [3, 4]. The primary cilium is an organelle that has been shown to have a role in controlling energy balance and glucose homeostasis [5]. Defects in primary cilia structure and function may result in the development of a wide range of diseases, collectively known as ciliopathies, with overlapping phenotypes including obesity and diabetes [5].

In this work, we aimed at studying the role of increased glucose levels in primary cilia assembly, as well as the role of primary cilia on cellular response to glucose-induced oxidative stress. For this, we supplemented the growth media of RPE-1 cells with different glucose concentrations (5 mM, 25 mM and 5 mM glucose + 20 mM mannitol). Cells were also induced to assemble primary cilia either before or after glucose supplementation. Using immunofluorescence microscopy (IF) we found that glucose supplementation did not affect the number of ciliated cells, cilia length was reduced in 25 mM glucose. We also evaluated, by IF, the nuclear levels of thioredoxin reductase 1 (TXNRD1), a major player in the oxidative stress response directly triggered by hyperglycemia [6]. We observed that TXNRD1 nuclear levels decreased when non-ciliated cells were subjected to the different supplemented concentrations of glucose. However, if cells were induced to assemble cilia before glucose supplementation the nuclear levels of TXNRD1 increased at 5 mM glucose, did not change at 25 mM glucose, or showed a smaller decrease at 5 mM glucose + 20 mM mannitol. If cilia assembly was induced after glucose supplementation TXNRD1 levels increased except for 5 mM glucose. Together, these results show that the presence of primary cilia dramatically affects the cellular response to glucose concentrations that probably induce oxidative stress.

**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 Instituto Politécnico de Lisboa IPL/2021/ObeCil_ESTeSL.

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# O12 From the lab bench to a clinical setting – CQE's Mass Spectrometry Lab in diagnosis

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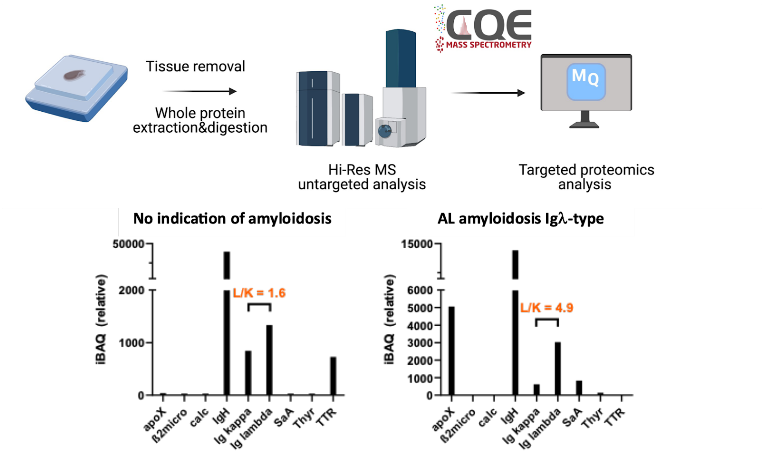
Plasma cell dyscrasias are at the origin of several diseases, such as myelomas. These diseases are characterized by a dysregulated monoclonal expansion of a given leukocyte type. The hallmark of these diseases is the aberrant overexpression and accumulation of one immunoglobulin chain in various tissues and organs – formation of amyloid deposits -, leading to successive organ failure and, when untreated or diagnosed at later stages, causing death. Classic clinical tools for amyloid diagnosis (staining for identification of amyloid presence and immunohistochemistry techniques for amyloid typing) require extremely costly and specific antibodies against human immunoglobulin chains; even so, clinical anamnesis is often indicative of amyloidosis but clinical assays turn out negative.

In this setting, CQE's Mass Spectrometry Lab has been collaborating with hemato-oncology clinicians in order to implement an MS-based approach to amyloid diagnosis. An HRMS-based bottom-up proteomics analysis of clinical biopsies, coupled to extensive bioinformatics data analysis, afford an accurate identification of deposited proteins, not only of the protein family but also of the sequence of the specific clonally expanded VDJ-recombination product.

Four clinical cases will be presented, corresponding to patients with a complete amyloidosis-suggesting history and negative histopathology results, for which it was possible to confirm clinicians' suspicions, and offer a complete amyloid profiling.

These four successful cases of pathology confirmation through MS tools demonstrate the impact of this technique in clinical settings and contribute significantly for the positioning of CQE's in clinical settings, where classical structural characterization tools are still seldom used.



**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 partially funded through FCT grants SAICTPAC/0019/2015 and PTDC/QUI-QAN/32242/2017 and through the Portuguese Mass Spectrometry Network (RNEM-LISBOA-01-0145- FEDER-022125).

# O13 Gold nanorods decorated with glycoporphyrins for combined cancer photodynamic and photothermal therapies

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Cancer is one of the leading health problems worldwide due to its mortality. In addition to conventional cancer therapies (surgery, radio-, chemo- and immune-therapies), other non-invasive therapies, with high precision and less side effects, have been studied in the last few decades such as photodynamic therapy (PDT) and photothermal therapy (PTT) [1,2]. The mechanism of action of PDT is based on the use of a photoactive compound (photosensitizer, PS) with light, at specific wavelengths, to generate reactive oxygen species (ROS) from the cellular oxygen. These ROS react with cell membrane and organelles, leading to selective cell death through apoptosis or necrosis [3,4]. The derivatization of the PS with biomolecules such as carbohydrates allows a targeted delivery strategy by recognition of uniquely expressed or overexpressed receptors on tumor cells, thus, increasing the selectivity of the treatment [5]. The combination of PS derivatives with photothermal agents (i.e., Au nanoparticles) allows to simultaneously perform PDT with PTT, especially under hypoxia, since the slight increase in temperature induced by the photothermal effect results in a higher treatment efficiency.

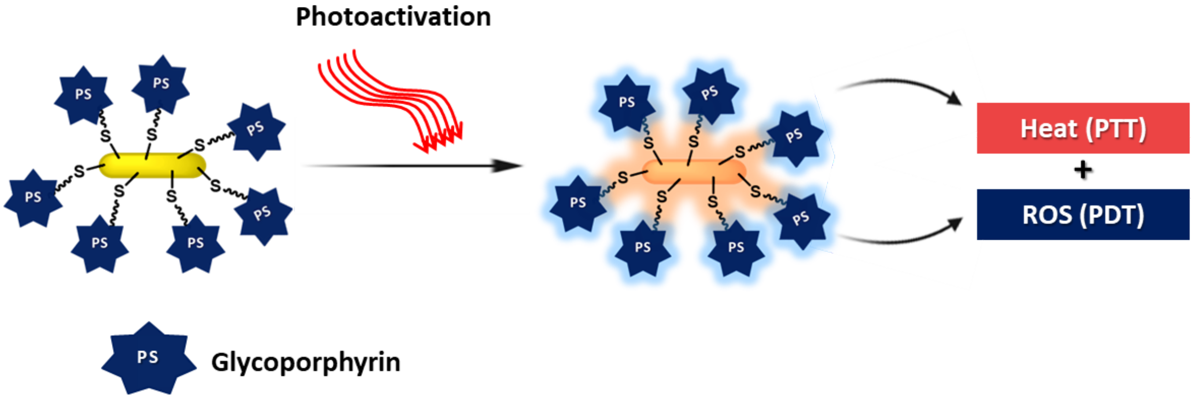

**Figure 1**. (Nano)formulation of bio-based AuNRs with glycoporphyrins

**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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# O14 Hunting metastatic breast cancer with novel ruthenium smart metallodrug delivery systems

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Breast cancer (BC) is still a major burden in society. There are 4 new cases and 1 death by BC every single minute, making it the most common and lethal tumour in women. Although treatable when early diagnosed, advanced or metastatic BC is incurable and patients face a median survival time of only 2 years, due to the lack of an effective therapy. Indeed, current treatments are unspecific, unable to reach BC metastases, and show severe adverse effects mostly due to poor selectivity for cancer cells over healthy tissues. This scenario claims urgency on finding a therapeutic solution [1].

Willing to provide society with a precision therapy for metastatic BC that overcomes the limitations of antineoplastic drugs in clinical use, our group is currently working on developing novel ruthenium smart metallodrug delivery systems (SMDS) capable of hunting both primary tumours and metastases of BC. These systems promote selective accumulation and controlled release of a cytotoxic complex of ruthenium 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 BC cells, tethered to a known ruthenium-cyclopentadienyl complex [2] 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**). Herein, we report on the synthesis of novel ruthenium SMDS through an innovative ultrasound-assisted solid-phase methodology, as well as their structural characterization and biological evaluation. The drug release profile of the SMDS was evaluated in solution at pH values that mimic the tumour microenvironment and the bloodstream/healthy tissues. Their cytotoxicity was assessed *in vitro* in a panel of human BC cells with different levels of FGFR expression. The new SMDS here presented showed high and selective antiproliferative activity against FGFR(+) BC cells, allied to controlled release of the cytotoxic ruthenium complex in its active form, suggesting potentially high value as prospective agents for precision therapy of metastatic BC.

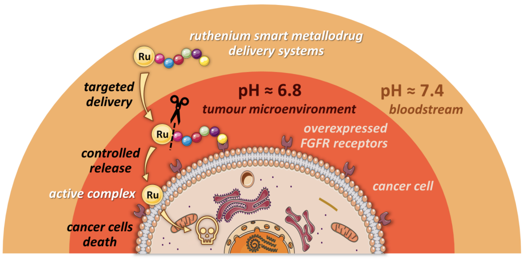

**Figure 1**. Proposed mechanism of action of the novel ruthenium smart metallodrug delivery systems.

**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 Ciências e Tecnologias Nucleares is a Research Unit funded by FCT through project UID/Multi/04349/2020. This work was also funded by FCT through project PTDC/QUI-QIN/0146/2020. J. F. Machado thanks FCT for his doctoral grant (SFRH/BD/135915/2018). T.S. Morais thanks FCT, as well as POPH and FSE-European Social Fund for CEECIND 2017 Initiative for the project CEECIND/00630/2017.

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# O15 Conjugation of tetrapyrrolic macrocycles with graphene quantum dots: Application and future challenges

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Photodynamic therapy (PDT) has been considered as a non-invasive treatment with less side effects when compared to conventional cancer treatments such as chemotherapy, radiotherapy and immunotherapy. In this therapeutic approach, the activation of molecules by visible or near infrared light irradiation at an appropriate wavelength in the presence of dioxygen is fundamental to generate cytotoxic reactive oxygen species (ROS), responsible by the oxidation of cellular constituents in the target tissue provoking the cell death. Ideally, the dyes, known as photosensitisers (PS), should be compounds with insignificant dark toxicity and some degree of hydrophilicity.

Among the high number of PS that have been studied in vitro and in vivo a special attention has been dedicated to porphyrins, corroles and phthalocyanines due to their high singlet oxygen yield, low toxicity and unique optical and electronic properties. However, the poor water solubility of tetrapyrrolic macrocycles can lead to formation of aggregates compromising their use in PDT.

To prevent aggregation, several studies have been focused on the incorporation of PS into nanomaterials such as carbon based nanomaterials. The development of conjugates based on corroles/porphyrins /phthalocyanines and carbon nanomaterials for cancer therapy is a recent topic of research with promising results found for graphene quantum dots (GQDs).

Graphene quantum dots (GQDs) possess excellent optical and electronic properties coupled with high photostability, aqueous solubility and biocompatibility. The presence of carboxyl and hydroxyl groups on their surface and edges enable covalent attachment, electrostatic interactions and hydrogen bonding with other suitable moieties [1]. In addition, the nonlinear optical response of GQDs presents great opportunities for the development of optical sensors operating in biological media [2].

In the present study GQDs have been conjugated covalently and non-covalently with tetrapyrrolic macrocycles (corroles, porphyrins and phthalocyanines). The optical and structural characterization of the resultant hybrid materials is discussed. Preliminary studies on cellular uptake and distribution, using confocal and multiphoton microscopy, are presented.

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# O16 Nanocatalyst-modified fibres for environmental remediation

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The water shortage and environmental pollution are major issues across the globe and have significant impact on our health and daily life and is one of the focus of the 2030 Agenda for Sustainable Development. It is urgent to address the water contamination problems in order to make available new technologies and materials capable of assisting in this challenge.

We have been using straightforward approaches for the modification of fibres with semiconductor nanoparticles displaying photocatalytic activity towards the degradation of pollutants in wastewater [1,2].

In this work, the successfully *in situ* immobilisation of crystalline nanoparticles (*e.g.* $TiO_2$, ZnO), on fibres, including carbon and glass, was confirmed by surface analysis, namely by diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM), **Figure 1**. The degradation of pollutants, such as pharmaceuticals, was tested under UV and visible light irradiation. The obtained results suggest that these hybrid materials are promising for application in environmental remediation as supported photocatalysts active under solar light.

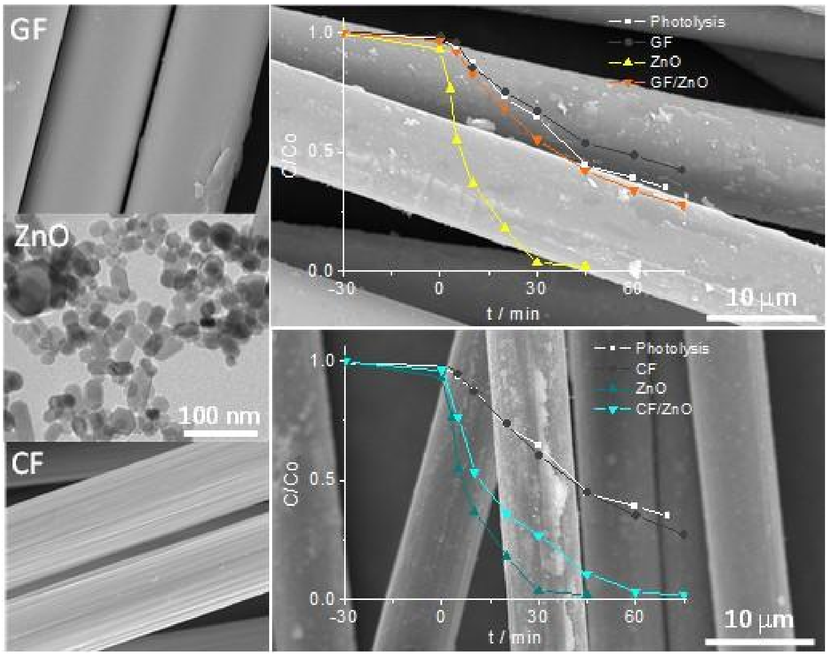

**Figure 1**. SEM images of pristine and ZnO-modified fibres. Inset: Time profiles for the photodegradation of pollutants.

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# O17 Magnetically-responsive photonic pigments from nanoparticle self-assembly in batch

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Structural color pigments offer time-resistant coloration brightness, contrarily to common dyes and pigments, that are prone to photobleach, loosing their color with time. [1] Furthermore, the addition of wide spectral absorbers such as iron oxide can enhance the color saturation of structural pigments by absorbing incoherent light scattering. [2]

Here, we present the synthesis of NEW magnetically responsive photonic supraparticles obtained by droplet emulsification, in a three-step procedure. First, magnetic nanoflowers with diameters around 30 nm (MNF) were prepared by a polyol-method .[3] Second, surface-charged polymer nanoparticles (PNPs) were prepared by batch emulsion polymerization with different diameters of ca. 194, 232 and 287 nm. [4] Finally, an aqueous dispersion of PNP (~16wt%) and MNF (0.12wt%) was injected into a jacketed glass reactor vessel containing hexadecane and SPAN80 (5 wt%) for droplet emulsification. The slow drying process of the aqueous droplets led to the self-assembling of the PNPs, yielding photonic structures with bright non-iridescent structural color. Furthermore, the magnetic nanoparticles improved the color saturation up to 200%, without affecting the structural integrity of the supraparticles. The incorporation of the MNFs resulted in magnetically responsive structural pigments, [5,6] with only a residual concentration of iron oxide.

Our magnetically-responsive photonic pigments can be produced from sustainable and environmentally friendly materials, using a batch method that can be easily scaled-up for industrial application.

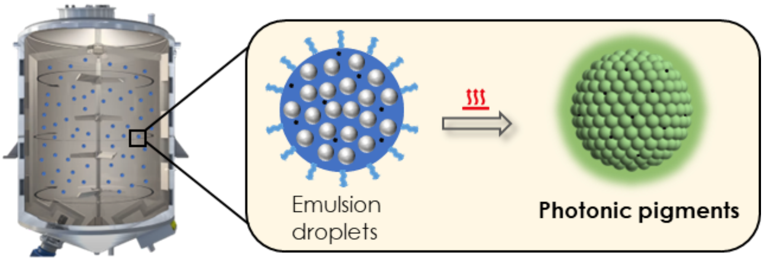

**Figure 1**. Droplet emulsification for photonic pigments assembling.

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# O18 Metrological assessment of composition trends of oceanic areas by Monte Carlo simulation of georeferenced information – Application to characteristic oceanic parameters

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The assessment of compositional differences over vast oceanic areas is highly dependent on factors such as seasonality, heterogeneity and size of the study area. The application of Monte Carlo Simulations has proved to be a useful tool to model and optimize the uncertainty associated to sampling in this type of systems [1,2] and infer about the probability density function (pdf) associated with the estimate of the average value of the determined parameters. When this pdf does not follow a normal behavior, the evaluation of composition differences in different periods must take into account its complexity. This study presents a methodology for comparing estimates of characteristic parameters of oceanic waters, such as nitrite, obtained under different seasonal conditions, which makes it possible to assess whether differences in composition, affected by sampling uncertainty, are significant or not. Two mean values are significantly different if the zero value is not between the 0.5 and 99.5 percentiles of the Monte Carlo simulation of the difference of mean.

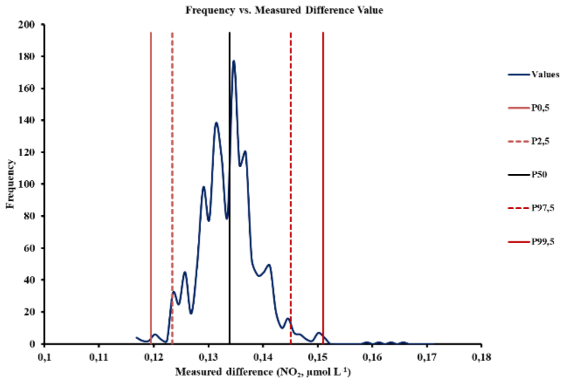

**Figure 1**. Simulated distribution of the difference in nitrite concentration, estimated from 20 random samples, obtained in two different seasonal conditions, in the studied Atlantic Ocean area; the mean difference value (P50), the P0.5, P2.5, P97.5 and P99.5 distribution percentiles are also presented.

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# O19 Solid-liquid-phase equilibrium: searching new systems for low temperature energy storage

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The incessant and constant increasing need for energy is requiring urgent and effective solutions. Renewable energies are intermittent, which often leads to a gap between the availability of energy and its demand. Therefore, energy storage becomes imperative for increasing the efficiency in the use of the produced energy. Concerning this, the use of phase change materials (PCMs) has taken a very important role, especially for active cooling systems. In particular, eutectic systems can be planned with characteristics that make them suitable for each application, allowing significant energy savings, which is very relevant in what concerns economic and environmental sustainability [1].

This work aims to the characterization of selected systems that can be used for energy storage at low temperatures, starting by the construction of solid-liquid phase diagrams using differential scanning calorimetry (DSC) results. Phase diagrams are crucial to characterize the behavior of these systems and reveals the robustness of the PCM, and for new PCMs, equilibrium studies enables to achieve the desired melting temperature [2].

A preliminary study was performed for the binary system $C_{10}$-$C_{12}$, aiming to assess the capabilities of the available equipment to characterize the solid-liquid phase diagrams at low temperatures. The test was able to reproduce with good quality the solid-liquid phase diagram obtained by Espeau [3] and later analyzed by Ventolà et al. [4].

Currently, the work has been focused on systems composed by di-n-alkyl adipates. One of those binary systems reveals to behave as a eutectic system at low temperatures. More recently, a binary system of di-n-alkyl adipates, has been studied being a promising system for thermal energy storage at low temperatures. This system has apparently a eutectic point around -32ºC, however it has a quite complex phase diagram which requires complementary techniques to better understand the solid-liquid phase equilibrium of this system. Details of this investigation will be described in the present communication.

**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. M.C.M. Sequeira acknowledges the PhD grant funded by FCT ref. UI/BD/152239/2021.

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# O20 Bar adsorptive microextraction (BAµE) applied to the determination of benzophenones in water matrices

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The occurrence of organic compounds in environmental matrices has been a topic of high interest in the scientific community since many are emerging environmental contaminants. These compounds can resist the treatment in Wastewater Treatment Plants and be later detected in the environment. A good example of this group of substances are benzophenones, which are additives used in cosmetics, pharmaceuticals, and personal care products as ultraviolet (UV) filters. UV filters can be found in environmental matrices such as wastewater, lakes, rivers, and coastal areas at low concentration levels (µg/L) [1,2].

The purpose of this study is the determination of benzophenones in environmental matrices through the development, optimization, and validation of bar adsorptive microextraction followed by analysis by high performance liquid chromatography with diode array detector (BAµE/HPLC-DAD) for the determination of 8 benzophenones in wastewater [3].

For the optimized experimental parameters, recoveries between 60 and 85% were obtained with limits of detection and quantification between 0.1 and 1.0 µg/L and between 0.33 and 1.33 µg/L, respectively.

The proposed methodology proved to be an alternative strategy for the analysis of benzophenones in environmental matrices, presenting as main advantages the use of small amounts of sample and solvent, easy handling, simplicity, and excellent analytical performance.

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# Poster Communications


MATSoft

# P1 Crystals, glasses, and gels: controlling solid state forms of simvastatin

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Simvastatin (**Figure 1**) is one of the most widely used active pharmaceutical ingredients (API) for the treatment of hyperlipidemias. The compound is employed as a solid in drug formulations. As such, particular attention must be given to the characterization of its different crystal forms (polymorphs), their stability domains, and the nature of the phase transitions that relate them. Modifications in crystal packing and crystallinity are commonly accompanied by significant changes in physical properties (e.g. variations in solubility), and may lead to serious problems in terms of reproducible preparation and safe use of a medicine. As a result, the characterization of structure−energetics relationships for solid APIs is of considerable importance in the pharmaceutical industry.

In this work simvastatin will be used as a model to illustrate how experimental (single crystal X-ray diffraction, hot stage microscopy, differential scanning calorimetry, and solubility measurements) and molecular dynamics results can be combined to guide the control of API production in specific solid state forms. Simvastatin has three known polymorphs. Form I is the thermodynamically stable one under ambient conditions and converts to the other two by fast solid−solid phase transitions (at 275.2 K for the form I → form II transition and 236.9 K for form II → form III). [1,2] Furthermore, long-lived amorphous phases of simvastatin have also been observed. [3]

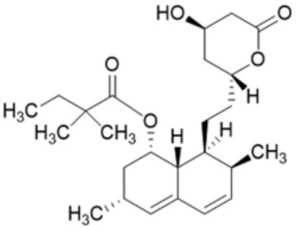

**Figure 1**. Molecular structure of simvastatin.

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# P2 The effect of alkali cation of the pseudocapacitive behaviour of δ-$MnO_2$

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Novel electrochemical energy storage devices have been encouraging the energetic transition from fossil fuels to renewable and cleaner energy by developing high power/energy density devices. Among these, $MnO_2$-based pseudocapacitors have been widely used over the past few years owing to their operation in eco-friendly aqueous electrolytes and exceptional electrochemical performance (100-400 F/g in a 0.9 V potential window) [1-3]. Two-dimensional (2D) birnessite, also known as δ-$MnO_2$, is a crystalline structure of $MnO_2$ known for its layered framework, with an interlayer spacing of ~ 7.2 Å, that promotes ion ($H^+$, $Na^+$, etc.) diffusion and enables the nanoconfinement of water molecules [4]. It is exactly this interlayer region that makes δ-$MnO_2$ so interesting as pseudocapacitor electrode, and hence tailoring the spacing between layers is essential to improve the electrochemical response of δ-$MnO_2$. One of the strategies is doping the structure with alkali cations that would act as pillars between layers and prevent distortion or collapse of the structure.

Having this in mind, in this work, we report a modified and low-cost co-precipitation strategy to synthesize birnessite-based materials with different alkali cations ($Li^+$, $Na^+$, $K^+$, $Cs^+$) that incorporate into the δ-$MnO_2$ structure, for electrochemical energy storage. X-ray diffraction (XRD) analysis revealed the birnessite signature with well-defined peaks assigned to 2D δ-$MnO_2$, and it was possible to observe the effect of the different cations on the interlayer spacing. The electrochemical performance of $K^+$-$MnO_2$ materials in 1 M $Na_2SO_4$ revealed superior capacitive behaviour in a wide potential window (~ 1.3 V), and high cycling stability of, at least, 80 % after 5000 continuous charge-discharge cycles. This exceptional behaviour towards energy storage was attributed to the increased $K^+$-$MnO_2$ interlayer spacing that enables the intercalation/deintercalation of electrolyte species, contributing to a more favorable diffusion of ions.

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# P3 Light propelled nanovehicles for drug delivery

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In the recent years, the interest in nanocarriers for controlled and intelligent drug delivery systems has increased due to the possibility to tune their morphology and properties. Nanovehicles offer extremely promising opportunities within this field. These can already address well very defined morphology, large cargo capacities, targeting of the destination, and on-demand controlled delivery.[1-6]

The goal of this project is to add self-propulsion capabilities to these nanovehicles, transforming them in versatile nanorobotic tools for drug delivery applications.

As proof-of-concept, traceable Janus nanoparticles (JNPs) will be prepared and will be composed by silica nanoparticles containing a fluorescent dye in the structure and a gold nanostructure in half of their outer surface. Irradiation of the gold nanoshell with near infrared light will generate a temperature gradient, propelling the JNP in the opposite direction of the gold nanoshell. The presence of a fluorescent dye in the silica nanoparticles allows to study the movement of the JNPs. The JNPs will be produced by a high yield process based on microparticle templating, specifically via a Pickering emulsion route.

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# P4 Cathodic electrodeposition of Fe-MOF-74 and derivatives

Reis, A. R.[A*]; Realista, S.[A]; Gomes, C. S. B.[B, C, D]; Ferraria, A. M.[E]; Corregidor, V.[F]; Alves, L. C.[F]; Martinho, P. N.[A]

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Purines play a major role in medical applications since their concentration levels translate into a useful diagnostic tool for some clinical disorders: gout, cardiovascular diseases, Lesch–Nyhan syndrome, or type 2 diabetes.[1] Therefore, the scientific community has been developing rapid, sensitive, and selective methods for the detection of these compounds. From all, metal-organic frameworks are a distinguished subclass of nanomaterials that take advantage of host-guest chemistry, potentially behaving as a sensor.[2] In this work, our group reports the synthesis of new ligands (Figure 1), characterised by nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR). These will be applied to the electrochemical fabrication of Fe-MOF-74 and derivatives thereof, characterised by FTIR, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), particle-induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS).

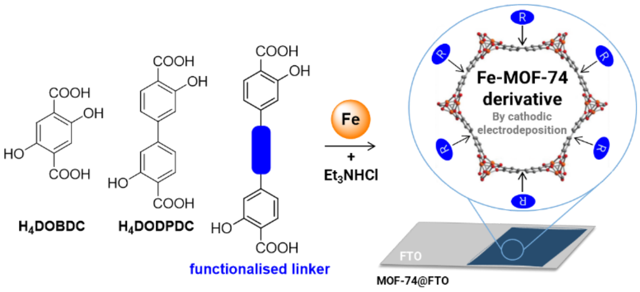

**Figure 1**. Fe-MOF-74 thin films and derivatives.

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# P5 Insights into solute-solvent interactions guiding crystallization from density measurements: the $OHC_6H_4C(O)R$ ($R = H, CH_3, CH_2CH_3$) family as a model system

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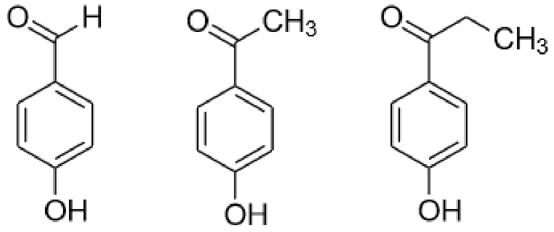
Crystallization from solution is arguably the most important process to obtain highly pure solid products [1,2]. There is still, however, very little knowledge about the early stages of crystallization (the pre-nucleation and nucleation stages) [3]. This is a major factor behind the lack of control over crystallization processes leading to manufacture problems related with polymorphism (the possibility of existence of two or more crystal forms of a molecule with different packing architectures). A particularly important open question within this scope, is how solute-solute and solute-solvent interactions determine the aggregation processes from which crystals emerge.

When evaporative crystallization is in view, insights into this question can be provided by density measurements as a function of concentration. This method was used in this work to investigate the aggregation/solvation of 4'-hydroxybenzaldehyde (HBA), 4′-hydroxyacetophenone (HAP) and 4′-hydroxypropiophenone (HPP) in ethanol (**Figure 1**).



**1** **2** **3**

**Figure 1**. Molecular structures of 4'-hydroxybenzaldehyde (1), 4′-hydroxyacetophenone (2) and 4′-hydroxypropiophenone (3).

In the case of HBA and HPP it was found that the apparent molar volume decreased as the concentration increased, until an approximately constant value was reached. An opposite trend was observed for HAP. This volumetric behavior results from a delicate balance between solvent structure breaking effects and solute-solvent H-bond interactions in very dilute solutions.

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# P6 Zn(II) coordination polymer for the effective removal of Congo Red dye

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The use of organic dyes in paper, textiles, plastics, rubber, coatings, etc. is widespread. Getting rid of harmful dyes before they are released into the natural system is an important issue from an environmental perspective [1]. Several methods have been developed for the removal of dyes from an aqueous environment, such as the use of activated carbon, filtration, photocatalysis, and adsorption. Some methods, such as activated carbon and filtration, however, are only effective for removing low levels of pollutants from water [2]. Thus, it is necessary to develop a type of material to overcome these difficulties that will reduce pollution caused by dyes while also achieving a high level of selectivity, as well as being able to be recycled.

In recent years, researchers have paid increasing attention to the area of designing of novel functional metal–organic frameworks (MOFs) or coordination polymers (CPs) due to their attractive properties, which include luminescence, magnetism, and catalysis applications [3-4]. Higher dimensional MOFs have also proven to be an excellent material for dye adsorption [5]. However, MOFs with low-dimensional structures exhibiting high dye adsorption are rare, but by promoting certain interactions, such as electrostatic connections, hydrogen bonding, and π-π interactions, this ability can be enhanced. We herein present the synthesis of a novel 1D Zn(II) CP that is effective in removing Congo Red dye (**Figure 1**). In silico studies have also been provided for an insight into the selective removal of Congo Red dye [6].

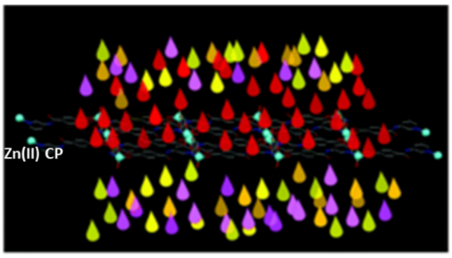

**Figure 1**. Showing the removal of CR dyes suing Zn(II) CP.

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# P7 Magnetic, luminescent and thermochemical properties of the $[C_2mim][Ln(fod)_4]$ series (Ln = Nd-Tm except Pm)

Cerdeira, A.C.[A]; Leal, J.P.[B]; Avó, J.[C]; Viola, C.[D]; Casimiro, M.H.[E]; Ferreira, L.M.[A]; Paz, F.A.A.[F]; Pereira, L.C.J.[A]; Pereira, C.C.L.[D]; Monteiro, B.[*G]

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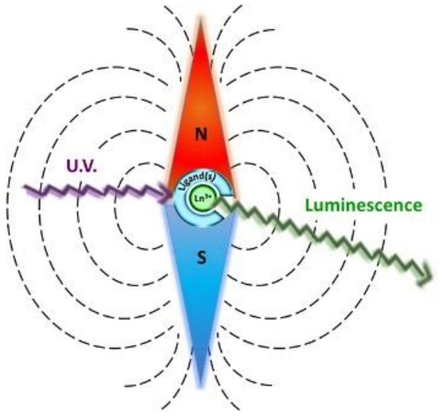
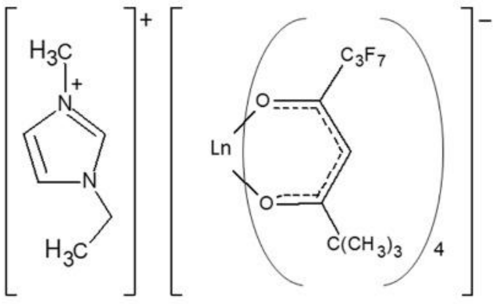
A series of nine Ln complexes of the type $[C_2mim][Ln(fod)_4]$ and their thermochemical, photophysical and magnetic susceptibility evaluated. Thermochemical studies presented a rare and reversible conversion between two solid phases, characteristic of the $[Ln(fod)_4]^-$ anion. The photophysical and magnetic studies revealed that the Dy and Er presented the multifunctionality of being simultaneously SMMs and Visible (Dy) or Near Infra-Red (Er) emitters. The Nd, Ho and Tm analogues present characteristic emission bands in the NIR region (800-1200 nm), while the Sm, Eu, Tb and Dy present emissions in the visible range. Magnetic susceptibility of complexes Tb, Dy, Ho, Er and Tm showed paramagnetic behaviour, although with different regimes, with Gd, Dy and Er presenting SMM behavior.





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# P8 Top-down or bottom-up, which pathway for synthesis of Carbon dots?

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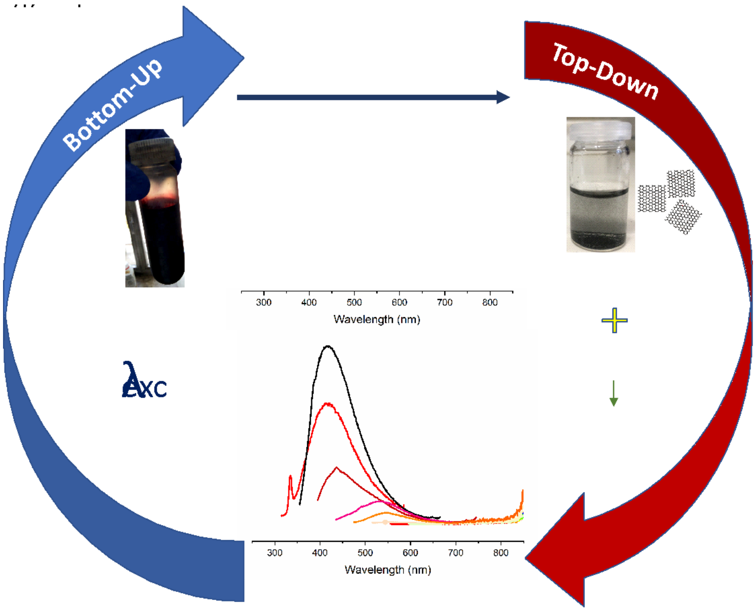
Carbon dots (CDs) are a class of nanomaterials that have attracted significant attention due to their chemical versatility, optical properties, conductivity, mechanical strength and can be applicable in diverse technological fields [1]. In particular, fluorescence emission of CDs in red region has always been the focus of research for biomedical and light-emitting devices applications. The optical properties of CDs are critically dependent on their structure (surface functionalization, doping, presence of defects on the carbon core, etc.) that is controlled by the synthetic approach. The purity of the final material is also an important issue affecting the optical properties.

In our group we have been producing CDs by bottom-up process achieved through the controlled pyrolysis or hydrothermal synthesis of urea and citric acid, regulating critical reaction conditions, such as temperature, solvent type and reagents ratio [2]. Top-down fabrication methods were also developed, where graphite was the carbon source and a hydrothermal method was adopted [3]. In this work, we build from this accumulated knowledge to tune the emission of CDs towards the red and improve the reaction yields and purity of the material. In the poster, strategic differences are highlighted, the optical properties are rationalized, and the search for more efficient separation methods is discussed. In addition, we address the main challenges and advantages of each method and discuss future progress.



**Acknowledgments:** Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e 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 work has been developed with the support of research projects PTDC/NAN-MAT/29317/2017, LISBOA-01-0145-FEDER-029319 financed by FCT and co-financed by the FEDER-POCI program.

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# P9 Tetracoordinate 9-borafluorenyl and diphenyl complexes of 8-hydroxyquinolinate chelating ligands: application in OLEDs

Fialho, Carina B.[A*], Rodrigues, Ana I.[A], Cruz, Tiago F.[A], Pander, Piotr[B], Dias, Fernando B.[B], Maçanita, António L.[A], Gomes, Pedro T[A]

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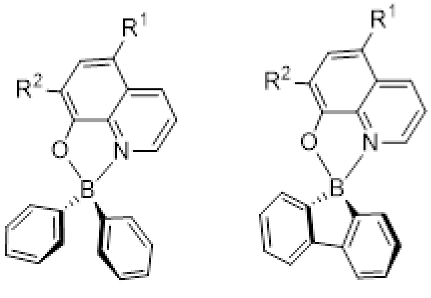
A path to harvest the triplet states of molecules generated under electric excitation, enabling high efficiency electroluminescence in organic light-emitting diodes (OLEDs), is the thermally activated delayed fluorescence (TADF). The conventional strategy to achieve this type of fluorescence involves a special architecture of the emissive molecule requiring a donor-acceptor (DA) orthogonal architecture, which may lead to a minimization of the energy gap between the charge-transfer singlet ($^1$CT) state and a local excited triplet ($^3$LE) state ($\Delta E_{ST}$, usually ≤ 0.2 eV). [1] With the aim of accomplishing an orthogonality between the two planar chromophores, a geometrical requirement to achieve delayed fluorescence, a group of tetracoordinate 9-borafluorenyl and diphenyl complexes of 8-hydroxyquinolinate chelating ligands containing different halogens as substituents have been synthesized (**Figure 1**). Herein, we report a series of organic light-emitting diodes (OLEDs) that were produced applying chromophores **3a**, **4a**, **4c**, **4d**, **4e** and **4f** in the emissive layers, in order to study the effect of halogenation on their electroluminescent properties.



4a-4h

3a-3h

**a** $R^1$=H, $R^2$=H
**b** $R^1$=F, $R^2$=H
**c** $R^1$=Cl, $R^2$=H
**d** $R^1$=Br, $R^2$=H
**e** $R^1$=Cl, $R^2$=Cl
**f** $R^1$=Br, $R^2$=Br
**g** $R^1$=Cl, $R^2$=I
**h** $R^1$=I, $R^2$=I

**Figure 1**. Tetracoordinate 9-borafluorenyl and diphenylboranyl complexes of 8-hydroxyquinolinate 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. We thank Fundação para a Ciência e a Tecnologia for the financial support Project PTDC/QUI-QIN/31585/2017 and Fellowship PD/BD/05622/2021).

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# P10 Nanostructured functional stone coatings

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Stones are one of the most abundant materials on earth, and also one of the most durable and secure natural materials. They have been widely used in historical and contemporaneous applications. However, the combined action of degradation processes due to natural and/or anthropogenic activity can change the properties of stone materials. The aim of this project is to develop nanostructured functional coatings to consolidate the stone and impart water and stain repellency properties. [1] The surface treatment should maintain or improve the appearance and chemical resistance of natural stone. Functional stone coatings with novel high performance features have the potential to help the industry increase the value of natural stone materials. In particular, water and stain repellence are features that could provide a competitive advantage to the stone industry.

This project will develop novel functional stone coatings based on the use of functional nanoparticles to provide the repellence properties. The stone surface treatment will be based on the use of alkoxysilane silica precursors optimizing the hydrophilic/hydrophobic character and adhesion to the surface of the stone. [2] The proposed process uses "green" technology, that is, of reduced environmental impact and low energy cost, and originates biocompatible materials. In addition to these properties the proposed production process is easily integrated into conventional stone surface treatment lines.

**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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# P11 Solubility control of theobromine *via* cocrystal formation

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A recent estimate indicated that ~70% of the most promising active pharmaceutical compounds (APIs) under development may fail due to solubility problems. The development of techniques to improve the solubility of an API without its chemical modification is, therefore, a pressing issue of major interest to the pharmaceutical industry. In the last decades, several approaches have been explored to address this problem, many of them involving the modification of the crystal structure of the substances. Among these, the use of co-crystals (the formation of crystals containing more than one molecule in the crystal lattice) is one of the most promising approaches.

This work describes the use of co-crystals to improve the solubility of the API theobromine (Figure 1), which is currently used e.g., as a heart stimulant, and to control fatigue and orthostatic hypotension. Co-crystallization was performed by mechanochemistry mixing the compound with hydroxybenzoic acids. The obtained mixtures were characterized by powder X-ray diffraction and differential scanning calorimetry. Finally, the solubility of the cocrystals was evaluated and compared with that of pure theobromine.

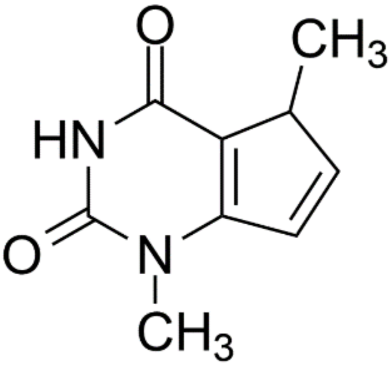

Figure 1. Chemical structure of theobromine.

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# P12 Tailor-made bifunctional polydopamine: polypyrrole co-polymers with adhesive and conductive properties

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Inspired by the mussel's adhesive nature, polydopamine (PDA) is a polymer that contains amine and catechol groups responsible for this property, with great application in surface coating, biomedicine, and nanotechnology [1,2]. However, its electrochemical use is limited, since it is a poorly conductive polymer or even non-conductive above a certain thickness (around 20 nm) [2,3], compromising, for example, its application in amperometric biosensors.

To overcome that issue, this work aims to explore the co-electropolymerization of dopamine (DA) with pyrrole (Py), a monomer that originates highly conductive polymers. Thus, it is expected to obtain a bifunctional polymeric film, that combines the adhesive properties of PDA, for further functionalization (*e.g.,* with biomolecules) and the high electronic conductivity of polypyrrole (PPy) [4] required for electron transfer events. The combination of those properties in a single polymer will have a great impact on the use of polycatecholamines for electrocatalytic and biosensing applications.

In this work, we optimized the potentiodynamic growth conditions of PDA/PPy co-polymer on a gold electrode, by adjusting DA/Py ratios, monomer concentrations, potential sweep rate and anodic limit potential. The co-polymer exhibiting the best electroactivity, showing redox conversions of both components, was achieved for 20 mM DA and 10 mM Py in a pH 6 phosphate-buffered saline (PBS) solution, for 10 cycles at 100 mV/s. Under such conditions, the electrosynthesized co-polymers proved to be thicker than pristine PDA films, as evidenced by electrochemical quartz crystal microbalance (EQCM), but still electroactive, allowing the electron transfer of both anionic and cationic species, such as $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$. It is worth noting that PPy grows significantly less than the co-polymer under the same experimental conditions, disclosing the synergetic effect of both monomers on the co-polymer electrosynthesis. The film's wettability was evaluated through contact angle goniometry, which demonstrates the film's hydrophilic properties ($\theta_{WCA} \approx 32°$), similar to PDA and different from PPy. Atomic force microscopy (AFM) provided the topography of the PDA/PPy film which, once again, most resembles a PDA surface, and also the polymer thickness. A value of 30 nm was obtained, which enables a high number of catechol moieties for further functionalization, within an electroactive and conductive film suitable for an electrochemical transduction matrix.

**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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# P13 Interfacial properties of mixtures of fluorinated and hydrogenated alcohols: Experimental and MD simulations

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The ability of fluorinated liquids to dissolve large quantities of respiratory gases, allied to their biocompatibility and chemical inertness and has triggered their potential use in biomedical and therapeutic applications such as perfluorocarbons-in-water emulsions for in vivo oxygen delivery (blood substitutes) and reverse water-in-PFC emulsions for pulmonary drug delivery in liquid ventilation. The knowledge of the surface and interfacial tension in presence of effective co-surfactants is obviously of utmost importance to control the stability and performance of both water-in-FC and in FC-in-water emulsions.

This work focuses on the study of interfacial properties of co-surfactants used to stabilize PFC/water emulsions. The interfacial properties of fluorinated alcohols and their mixtures with the corresponding hydrogenated alcohols have been investigated by three complementary techniques: experimental, Molecular Dynamics (MD) simulations and soft-SAFT-DGT calculations.1 The surface tension of the pure fluorinated alcohols was measured as a function of temperature. The liquid-vapour surface tension of the mixtures was measured as a function of composition. Interestingly, most mixtures display aneotropes, i.e., minima in the surface tension vs composition curve, which is a very unusual behaviour. The water-liquid interfacial tension of binary mixtures was also experimentally measured. MD simulations were performed to obtain a molecular level insight of the structure of the bulk and interface.

The abstract should be prepared following the guidelines provided in this template. It should be structured in order to make reference to the most relevant results previously found, to the most significant findings and finally to the conclusions related to the contribution.

**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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# P14 Hybrid silica nanoparticles for formaldehyde-scavenging in high performance resins

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Urea-formaldehyde resins (UFRs) have seen an increased growth in usage ever since their discovery and subsequent industrial production, in the first half of the XX century [1]. Nowadays, this use as a strong adhesive has made these types of resins an important part in the production of wood composites. These adhesives show great competitive advantages, both economically and performance-wise, however a big drawback in utilizing UFRs is the subsequent emission of formaldehyde after the curing process.

Formaldehyde, one of the components of UFRs, has been classified by the International Agency for Research on Cancer (IARC) as a carcinogen [2], with other symptoms, such as skin and eye irritation at higher concentrations of exposure. One solution to avoid formaldehyde emissions is the use of scavenger smart nanomaterials.

Silica nanoparticles (SNP) are a great option for scavengers as they show remarkable versatility in functionalization, size and structure, and a high surface area [3].

The purpose of this work is to develop SNP scavengers, synthetized using the Stöber method [4], containing amine groups that react with free formaldehyde, capturing it and therefore reducing its emission. For the implementation of a smart system, two types of SNPs were synthetized: one with a core of silica functionalized with amine groups; the other, with an added silica shell without the amine groups, to act as a barrier to formaldehyde capture before the curing process.

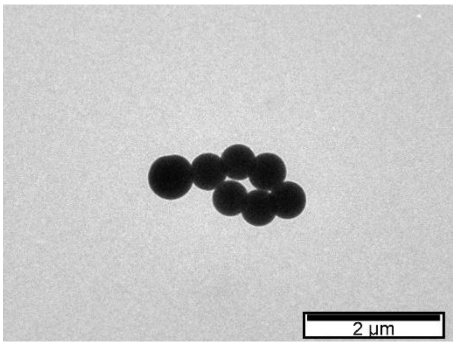

**Figure 1**. TEM image of synthetized amine-functionalyzed silica nanoparticles with a mean diameter of 582 ± 38 nm.

**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. Financial support from FCT, project SafeR (PTDC/CTM-COM/1581/2021)

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# P15 Mesoporous nanoparticles with a dual pore system based in stimuli responsive templates for selective control release

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Mesoporous silica nanoparticles (MSNs) are exciting materials due to their high internal surface area and pore volume, tunable pore size, colloidal stability, and the possibility to selectively functionalize the inner (related with 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.

MSNs with a dual pore system have two distinct types of pores that can interact independently with two different cargos at the same time in a single particle, which presents great prospects in areas such as catalysis, sensing, energy, biomedicine, etc [1].

Although some attempts have been made to developed silica nanoparticles with two different pores morphology, in all cases the templates used for the formation of the mesoporous structures were removed at the same time [2]. This represents a problem since the selection of templates used to produce dual-pore system MSNs should take into consideration that they should be removed selectively to allow preferential pore functionalization and selective control release.

An innovative strategy to produce dual-pore system MSNs is presented in this work based on a system of two surfactants, which includes a smart surfactant that can be selectively removed using a specific stimulus [3]. Two possible structures for the smart surfactant are proposed in this work, as well as structures for the inert surfactant, to satisfy the necessary requirements for the successful production of dual-pore system mesoporous silica nanoparticles.

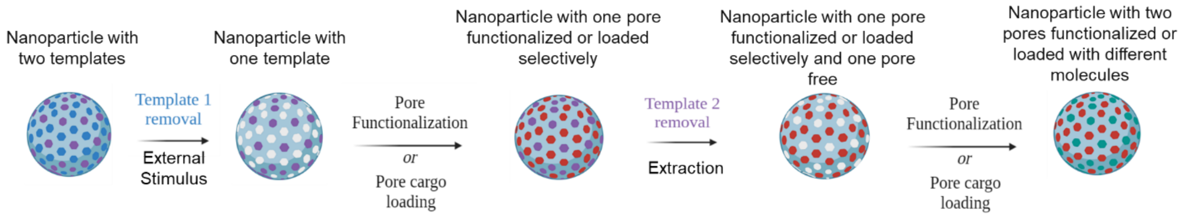

**Figure 1**. Schematic representation of the strategy devised to produce a dual pore system MSN. Through the selective removal of each template, the pores can be functionalized or loaded with a different cargo.

**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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# P16 Multiresponsive and reversible photonic supraparticles for colorimetric sensors

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The stimuli-responsive and dynamic color changes displayed by a variety of organisms are a particularly attractive material property for sensing and signaling applications in chemistry, biomedicine, mechanics, etc.

Responsive photonic crystals (RPCs) exhibit dynamic structural color changes through reversible adjustment of their own photonic stop bands (PSB) under specific conditions, that can be varied through control of the refractive index or lattice spacing. RPCs can respond to various external stimuli such as temperature, solvent, pH, humidity or pressure, among others and show great potential in color displays, biological or chemical sensors, and other optically active based systems. Among the various stimuli mentioned, temperature is one the most exploited due to the unique properties of polymers such as poly(N-isopropylacrylamide).

Here, we aim to develop multiresponsive and reversible photonic supraparticles for application as colorimetric sensors. The photonic supraparticles will be assembled by droplet emulsification of aqueous dispersions of core-shell polymer nanoparticles composed of a hard core made of polystyrene (PS) or poly(methyl methacrylate) (PMMA) and a soft shell of poly(N-isopropylacrylamide)-*co*-poly(acrylic acid) (PNIPAM-*co*-PAA). The nanoparticles shell is responsive to temperature, pH and ionic strength, so that the photonic supraparticles structure will be also stimuli-responsive, thus producing a change in color (Figure 1). [1, 2]

The change in color reflected by the photonic supraparticles upon temperature, pH and ionic strength stimuli will be evaluated using the intensity and position of the Bragg diffraction peak. [3]

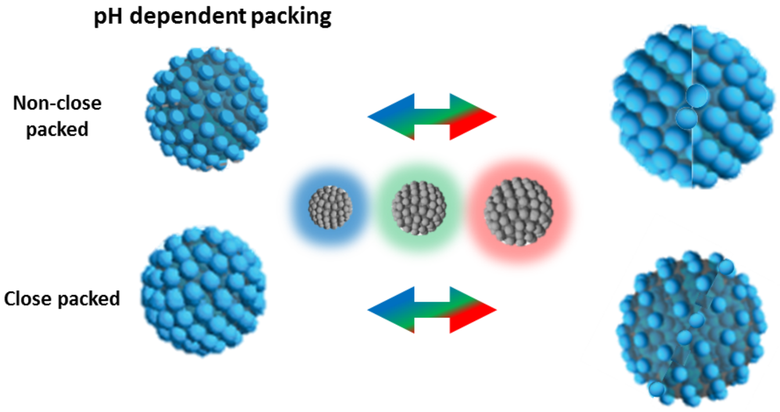

**Figure 1**. Temperature controlled dynamic color change characterization of photonic supraparticles with different polymer nanoparticles arrangement (assembled at different pH and ionic strength).

**Acknowledgments:** Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e 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.

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# P17 Zinc oxide mesoporous nanoparticles for advanced applications

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The importance of zinc oxide nanoparticles has growth in the last years due to the high potential of this material in applications such as catalysis, sensors, drug delivery, and optoelectronics.

The goal of this project is to develop new synthetic strategies for the preparation of zinc oxide mesoporous nanoparticles for advanced applications. Taking advantage of the know-how in our group on the preparation of other metal oxide nanoparticles, [1-3] this project will develop new synthetic strategies through the rational selection of the components (zinc source, template) and reaction conditions (pH, temperature). The new zinc mesoporous nanoparticles with precise properties (particle diameter with low dispersity, pore width and geometry) will open new opportunities for the application zinc oxide-based nanomaterials.

**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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# P18 Formaldehyde-scavenging nanoparticles for high performance resins

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Urea-formaldehyde resins (UFRs) are a class of thermosetting resins comprising nearly 80% of the total amino resins manufactured worldwide [1].

Formaldehyde emissions from UFRs are a major problem in the wood-based panels industry. Its release is either due to non-reacted formaldehyde or to resin hydrolysis.The present limit to formaldehyde emissions is 8 mg/100 g in dry board [2].

The purpose of this work is to develop polymeric nanoparticles that have a scavenge the unreacted formaldehyde in UFRs. Nanoparticles are stimuli-responsive, being activated by the temperature and pressure increase during the resin hot press cure. The benefits of the introduction of these polymer nanomaterials in the board industry are numerous: minimization of the formaldehyde emissions, longer shelf-life for the urea-formaldehyde resin and better mechanical properties of the wood-based panel.

**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. Financial support from FCT, project SafeR  PTDC/CTM-COM/1581/2021.

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# P19 Hemimicelles of semi-fluorinated alkanes: molecular origin and function as self-assembled templates for nanomaterials applications

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Semi-fluorinated alkanes (FnHm, $C_nF_{2n+1}C_mH_{2m+1}$) are diblock molecules formed by a hydrogenated chain bonded to a perfluorinated segment, which are both hydrophobic and mutually phobic. These primitive surfactants, lacking a polar head, form Langmuir films at the surface of water and some solid substrates [1,2]. The films are formed by discrete, mono-dispersed hemimicelles, hexagonally packed in 2D lattices, which are attractive for the bottom-up fabrication of self-assembled templates and nano-patterned surfaces. Recently, the formation, structure and size of F8H16 hemimicelles was elucidated by Molecular Dynamics (MD) simulations [3]. The spontaneous organisation in dense surface aggregates is typical of the fluorinated moieties, a phenomenon which happens even at very low surface density [4].

In this work, we use MD simulations to systematically characterise other FnHm systems. The pit in the centre of the hemimicelles is uncovered to result from the alignment of the $CH_2$-$CF_2$ dipoles. The diameter of the hemimicelles is found to be a function of the chain lengths of the CF and CH moieties. The results are in remarkable agreement with experimental data. Our findings were rationalised developing a model relating the geometry of the molecules with the size of the hemimicelles, in a fully predictive way. The influence of different substrates and additives in the water subphase (electrolytes and small organic molecules), on the stability and structure of the hemimicelles is also studied. The potential to selectively store different additives within the cavities of the hemimicelles is envisaged.

These results demonstrate, for the first time, that the morphology of the FnHm hemimicelles is determined by the molecular dipole and the length of the hydrogenated and perfluorinated segments, providing an overall understanding of the self-assembling process.

**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. P.S acknowledges funding from FCT in the form of a PhD grant SFRH/BD/149192/2019.

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# P20 Production and characterization of an ultralight metallic structure by chemical deposition on a sacrificial polymeric matrix

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The goal of reducing weight from structural components in vehicles and aircrafts has always been a key research point in the automotive industry. On this quest, the HRL Laboratories developed, in 2011, the first Nickel-Phosphorous Microlattice that had up to 99.99% of volume porosity, aiming to replace bulk structural materials of aircrafts [1]. This research is focused on the production of Ultralight Metallic Nickel-Phosphorous Microlattices through electroless deposition process onto an Acrylonitrile-butadiene-styrene (ABS) sacrificial matrix. The production of these structures used the Fused Filament Fabrication (FFF) method, differing from the typical use of the Self-Propagating Polymer Waveguide (SPPW) technique and its photopolymeric resins. The produced structures weighted around 1-1.4 g and had densities and relative densities ranging from 30-42.5 Kg/m$^{-3}$ and 0.34-0.48%, respectively. The microlattices were mechanically tested to study their Compressive Young Modulus, maximum stress and strain values, as well as their deformation behavior, structural defects, and strain recovery ability. The use of the FFF technique proved to be a viable option for the production of the sacrificial polymeric template and the compression tests showed very interesting results, revealing the potential of both the structures and the production method.

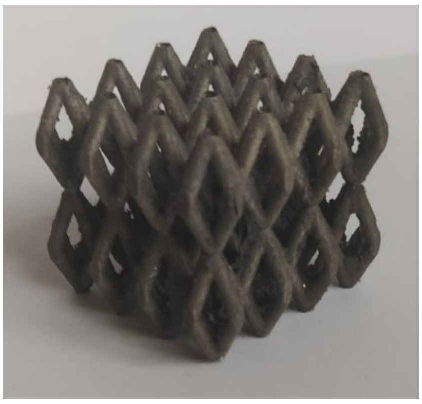

**Figure 1**. Final Nickel-Phosphorous Microlattice obtained from the production method developed.

**Acknowledgments:** Would like to thank Marco Leite, Manuel Sardinha and João Ajuda from the IDMEC, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal, for helping with the additive manufacturing of the polymeric template; and Sérgio Gonçalves from the IDMEC and the Biomechanic Lab, Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisboa, Portugal, for helping with compression tests of the Microlattices.

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# P21 A 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 forms of boric acid and phenylboronic acid, in aqueous media (**Figure 1**).

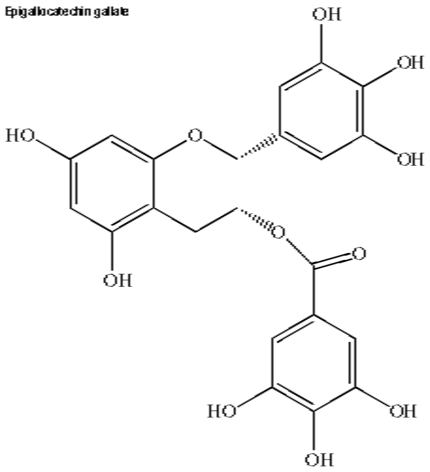

**Figure 1**. Structure of epigallocatechin gallate, here studied as a possible boron sensor.

**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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# P22 Ca-looping process for $CO_2$ capture from industrial flue gas using CaO-based sorbents

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The cement industry is responsible for 8 % of global anthropogenic $CO_2$ emissions to the atmosphere [1]. Among carbon capture technologies, Ca-looping is considered a promising process because it allows a high theoretical $CO_2$ capture capacity (0.78 g $CO_2$/g CaO), high selectivity and the advantage of using the purged sorbent as raw material in the cement production [2]. In this study, different CaO-based sorbents such as limestones and waste marble powders, were tested in a Fluidized Bed Reactor laboratory scale unit to evaluate the sorbents $CO_2$ capture capacity, through ten carbonation-calcination cycles (calcination: 930 ºC, 70 % $CO_2$; carbonation: 700 ºC, 15 % $CO_2$). To evaluate the effect of contaminants on sorbents $CO_2$ carrying capacity, the carbonation was performed using two distinct carbonation gas atmospheres: real industrial flue gas from a cement plant, and a synthetic gas mixture with the same $CO_2$ composition of the real flue gas (15 % of $CO_2$ in air). The sorbents showed a better performance for $CO_2$ capture from the real flue gas due to the presence of moisture in the flue gas used. Changes in the textural properties of sorbents can justify the improved performance observed.

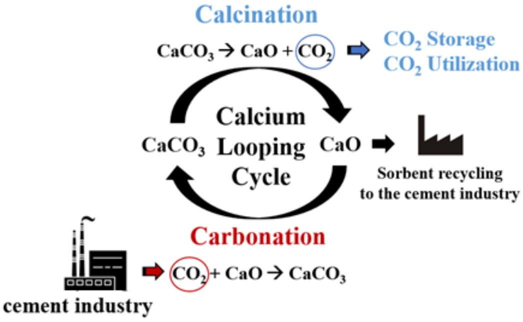

**Figure 1**. $CO_2$ capture by Ca-looping integration in a cement industry.

**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. $c^5$Lab – Sustainable Construction Materials; Instituto Superior Técnico/Universidade de Lisboa. CERENA is a Research Unit funded by FCT through projects, UIDB/04028/2020, and UIDP/04028/2020 "SoCaLTES - Solar-driven Ca-Looping Process for Thermochemical Energy Storage" [ PTDC/EAM-PEC/32342/2017]. $c^5$Lab - Sustainable Construction Materials' Association is a collaborative laboratory co-financed by:

Lisb@20²⁰ CENTRO 2020 PORTUGAL 2020 UNIÃO EUROPEIA Fundo Social Europeu

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# P23 Iron complexes and coordination polymers for magnetic sensing materials

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Magnetic systems combining their spin lability with the effect of optical rotation, are very attractive and studied under the hot topic of magnetic dichroism. This effect is centered around the combined effect of optical rotation and magnetic behavior in a molecule, when exposed to unpolarized and polarized light beams, which can show promising applications as magnetochiral molecular sensors [1]. Here, we report the synthesis and characterization of bidentate and tridentate ligands, Figure 1, and the magnetic properties of their Fe(II) and Fe(III) complexes. While the Schiff-base ligand preferably forms discreet Fe(III) complexes, the other two form coordination Fe(II) polymers [2,3].

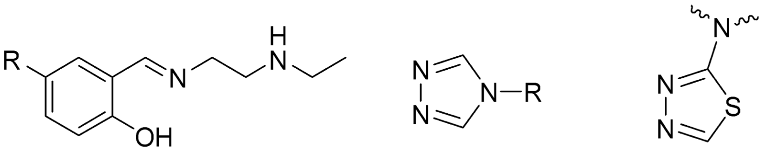

**Figure 1**. General structures for the organic ligands synthesised in the project.

**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). S.R. acknowledges FTC for financial support (2020.02134.CEECIND).

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# P24 Microscale designs towards light triggered processes in a capsule

Vaz Serra, Vanda[A*]; Serra, Sofia[A]; Charana, Tiago[A]; Paulo, Pedro[A]; Vallejo, Mariana[B]; Moura, Nuno[B]; Neves, M. Graça[B]; Trindade, Dário[C]; Vieira, Sandra[C]; Costa, Sílvia[A]

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In recent years, polyelectrolyte microcapsules (PECs) have received a great deal of attention due to their possible use as drug delivery systems, biosensors, and micro-reactors. The integration of light-absorbing molecules such as porphyrins, within these platforms enables the production of optically addressable devices [1-3]. Porphyrins are recognized photosensitizers for cancer treatment and diagnosis, due to their intrinsic ability to generate cytotoxic oxygen species and to emit in the red or near infrared when exposed to visible light. Nevertheless, most porphyrins are weak emitters, have solubility issues, and tend to aggregate in water.

Herein we report some of the recent advances regarding PECs design and functionalization aiming to improve light triggered processes across polyelectrolyte shells. It is shown that the rational assembly of cores, dyes and polyelectrolyte multilayers are the key parameters that rule pH-controlled porphyrin adsorption and release [2]. Further, PECs were also employed as micro-reactors for the construction of needle like porphyrin J aggregates [3]. Recently, we have shown that PECs are valuable platforms towards the preparation of spectrally engineered microsystems for efficient plasmonic fluorescence enhancement of porphyrins [4]. Fluorescence lifetime imaging microscopy of porphyrin-nanogold PEC hybrid data reports a notable $10^5$–$10^6$-fold increase in the maximum detected photon rates from diffraction-limited spots and an overall six-fold increase in fluorescence as averaged over the whole microcapsule area. The cytotoxic activity of porphyrin-nanogold PECs hybrid in HeLa Cells originating from human adenocarcinoma, will also be shown, and discussed.

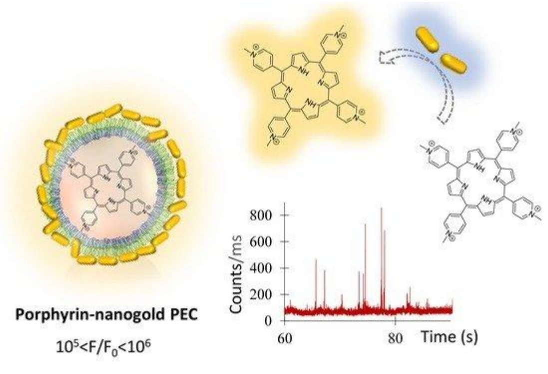

**Figure 1**. Microscale design towards light triggered processes: fluorescence enhancement on porphyrin-nanogold PECs hybrid.

**Acknowledgments:** Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e 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 research was funded by FCT through projects PTDC/QUI-COL/29379/201 and IDB/50006/2020.

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# P25 Determination of the enthalpy of sublimation of the caffeine polymorphs

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The study of the crystalline structures of a substance and their physical properties is an important field of research with applications in the development of new medicines, explosives, paints, and electronics [1]. Thus, it is important to develop the ability to predict the properties of crystal forms of a compound (e.g., different polymorphs where molecules are assembled with different packings), to design materials with optimal properties for a given application. Promising methods to achieve this goal include the use of computational techniques, like molecular dynamics simulations. These are based on intermolecular force fields, which, employing simple atom-atom interaction potentials, can be used to predict many properties of materials. However, due to the empirical nature of these force fields, they need to be validated against benchmark experimental data, like molar enthalpies of sublimation ($\Delta_{\mathrm{sub}}H^{\mathrm{o}}$) and crystal structure unit cell parameters [2]. Although results of this type can be found in the literature, $\Delta_{\mathrm{sub}}H^{\mathrm{o}}$ data that can be safely assigned to specific crystal structures are rarely found. This may be one of the main causes of the discrepancies often found between $\Delta_{\mathrm{sub}}H^{\mathrm{o}}$ values reported by different authors. Thus, the development of a benchmark database of enthalpies of sublimation for specific crystal structures of materials is a crucial step for the development of theoretical methods. With this objective in mind, this work describes the revaluation of the enthalpy of sublimation of the different polymorphs of caffeine (Figure 1), to which previous results span a range of ~10 $\mathrm{kJ \cdot mol^{-1}}$ [3]. The experiments were performed by Calvet microcalorimetry using samples characterized by powder X-ray diffraction and differential scanning calorimetry.

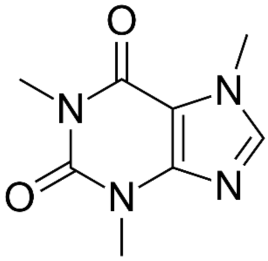

**Figure 1**. Molecular structure of caffeine.

**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 project PTDC/QUI-OUT/28401/2017 (LISBOA-01-0145-FEDER-028401) and by the FCT-DAAD program for cooperation in science.

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# P26 PVA-based hydrogels for cartilage replacement with local anti-inflammatory action

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The replacement of cartilage damaged areas can be performed using natural or synthetic materials with properties similar to articular cartilage. Hydrogels like polyvinyl alcohol (PVA) present mechanical properties similar to articular cartilage, low friction coefficients and capacity of anti-inflammatory drugs incorporation [1]. This work aims to develop PVA-based hydrogels with improved mechanical and tribological properties and ability to ensure a controlled diclofenac release.

Hydrogels of PVA, PVA/PAA (PVA mixed to PAA (polyacrylic acid)), PVA/PAA+PEG (immersion of the previous hydrogel in 100% PEG (polyethylene glycol)) and PVA/PAA+PEG+A (annealing of the latter hydrogel) were produced by freeze-thawing method. Their swelling behavior, mechanical properties, wettability, morphology and friction coefficient were accessed. The diclofenac release ability was studied for the best performing hydrogel, as well as its cytotoxicity.

The results showed that while the addition of PAA increased the swelling capacity, PEG-doped and annealed hydrogels presented comparable, but lower swelling values than PVA. All hydrogels were hydrophilic. PAA hydrogels presented lower tensile tangent modulus and ultimate tensile strength than PVA, while PEG and annealed hydrogels showed higher elastic modulus, elongation-to-break, tensile strength, and toughness. In compression tests, PVA/PAA presented the smallest elastic modulus, while for PVA/PAA+PEG and PVA/PAA+PEG+A no significant differences were observed relatively to PVA. Regarding morphology, it was found that PEG and annealed hydrogels led to less porosity. While PVA/PAA presented the highest friction coefficient, PVA/PAA+PEG+A led to the lowest values. PVA/PAA+PEG+A was selected for drug release studies due to its better performance. A significant improvement in the diclofenac release profile was observed, showing a sustained release for ~3 days. Also, it was demonstrated that this hydrogel does not induce lysis, hemorrhage or coagulation.

In conclusion, PVA/PAA+PEG+A was the best performing material, revealing a controlled release for more than 3 days, without presenting any irritant behavior for the biological tissues.

**Acknowledgments:** To Fundação para a Ciência e a Tecnologia (FCT) for funding through the project PTDC/CTM-CTM/29593/2017 (CartHeal) and the unit projects UIDB/00100/2020 (CQE), UIDB/04585/2020 CiiEM), UID/CTM/04540/2020 (CeFEMA) and UIDB/50022/2020 (IDMEC/LAETA, and for the PhD grant of A.S. Oliveira (PD/BD/128140/2016) and A.C. Branco (SFRH/BD/145423/2019).

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# P27 Therapeutic contact lenses for the simultaneous release of drug and peptides to the back of the eye

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To avoid the need of intraocular injections, several strategies have been investigated to improve the permeation of topical drug delivery to posterior segment of the eye, such as the use of peptides as drug carriers. KTPNH$_2$, a derivative of Kyotorphin, and Penetratin (Pen) were previously designed to increase membrane permeability.

Herein, the possibility of producing therapeutic contact lenses, simultaneously loaded with Dexamethasone Sodium (DexSod) and either KTPNH$_2$ or Pen, was evaluated with the aim of increasing the delivery efficiency of DexSod to the back of the eye.

First, *ex vivo* tests, performed with vertical Franz diffusion cells on isolated porcine conjunctivas, revealed an increased permeation of DexSod across the porcine conjucntiva in the presence of Pen. HEMA-based hydrogels (H) were investigated as potential contact lens backbone. Autodock software was used to identify the monomers acrylic acid (AAc) and aminopropyl methacrylamide (APMA) able to interact with the peptides and DexSod, respectively. Hydrogel discs (N ≥ 3) were loaded by soaking in a dual solution of peptides and drug. Drug-release was performed *in vitro* in sink conditions (**Figure 1**).

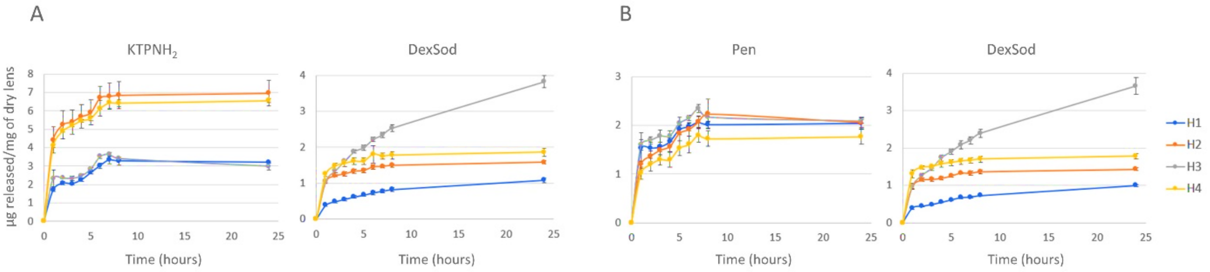

**Figure 1**. Simultaneous release of KTPNH$_2$ and DexSod (A) or Pen and DexSod (B) from HEMA-based hydrogels: H1 (HEMA), H2 (HEMA+AAc), H3 (HEMA+APMA) and H4 (HEMA+AAc+APMA).

A simultaneous release of the peptides and DexSod for at least 8 hours was obtained, which is compatible with the wearing time of daily contact lenses. AAc (H2 and H4) improved the delivery of KTPNH$_2$, while APMA (H3) significantly improved the release profile of DexSod. In hydrogels containing both functional monomers, the effect of APMA on the release of DexSod was not significant.

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# P28 Effects of non-conventional sterilisation methods on PBO-reinforced PVA hydrogels for cartilage replacement

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Articular cartilage degradation is a recurrent pathology that affects millions of people worldwide. Being an avascular tissue, it has limited healing capacity, and current therapeutic strategies show several limitations [1]. Hydrogels have gained great attention as possible cartilage substitutes, due to their biocompatibility and high-water contents. Poly-vinyl alcohol (PVA) is considered one of the most promising hydrogels, however its mechanical properties hinder their application [2]. Reinforcement of the PVA is required and can be achieved through the addition of nanofibres to the hydrogels' polymer network. An interesting polymer for this application is poly(p-phenylene-2,6-benzobisoxazole) (PBO), as this synthetic fibre shows high tensile strength (~5.8 GPa), and a compressive strength ranging ~0.5 GPa [3]. In this work, a PVA hydrogel, reinforced with PBO nanofibres, obtained by cast-drying, underwent three non-conventional sterilisation methods (i.e., microwave irradiation, high hydrostatic pressure (HHP) and argon plasma glow discharge) in order to avoid problems in polymer properties associated with common sterilisation methods. The efficacy of sterilisation on the natural bioburden, in the chosen conditions, was accessed and the synthesised hydrogels were characterised in terms of their structural and mechanical properties, wettability, swelling capacity and rheological behaviour, to evaluate possible effects due to the sterilisation procedures. Finally, biocompatibility of the hydrogels was ascertained via irritability and cytotoxicity assays. All used methods proved to be capable of sterilising the material but led to changes in its properties. Microwave irradiation increased the amount of double bonds which improved the tested mechanical and tribological properties. HHP increased single bonding, which improved the tested properties, except the compressive stiffness at high loads. Plasma treatment resulted in breakage of bonds, thus decreasing the PVA-PBO's tribological and load bearing capabilities but improved both the tensile and shear resistance. None of the sterilisation methods induced irritability and cytotoxicity. PVA-PBO hydrogels after microwave irradiation proved to be the most promising materials for cartilage substitution.

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# P29 Mechanistic and energetic insights into the formation of maleic acid: L-Phenylalanine co-crystals with 1:1 and 1:2 Stoichiometries: Thermodynamic and time-resolved *in situ* synchrotron X-ray diffraction and studies

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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 and chemical properties of organic materials without compromising their function. A widely used synthetic route to obtain organic co-crystals is through mechanochemistry, which uses mechanical energy to promote the combination of two or more solid precursors in a single crystal lattice. The mechanistic aspects of the process have been, however, very little explored. Synchrotron X-ray diffraction has proved to be a very powerful methodology to obtain this kind of information. [1] Here we describe a real-time *in situ* SXRD study of the mechanism of formation of maleic acid-L-phenylalanine co-crystals with 1:1 and 1:2 stoichiometries. The characterization of this process on thermodynamic grounds using calorimetry and solubility measurements will also be addressed. [2]

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# P30 Improved corrosion resistance and bioactivity of Mg-2Ca alloy with $TiO_2$ nanoparticles embedded in a polycaprolactone (PCL) coating

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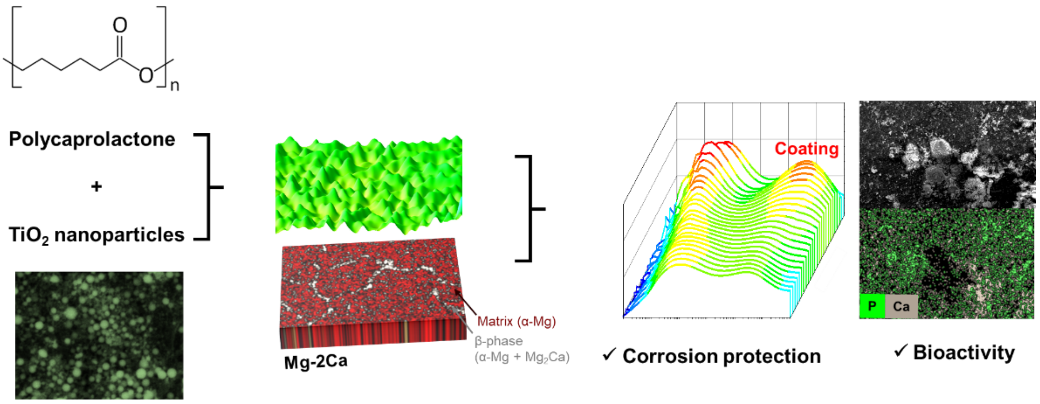
When seeking bone healing applications, calcium (Ca) is the preferred element for Magnesium (Mg) alloying. Unfortunately, the fast degradation rate of these alloys impairs their applicability as bioresorbable implantable. To overcome this limitation, the design of biodegradable polymeric coatings was made with polycaprolactone (PCL). TiO2 nanoparticles (NPs) were embedded in the polymeric matrix to further increase the protectiveness and bioactivity of such coatings. The degradation rate, assessed by electrochemical impedance technique (EIS) in cell culture medium proved the superior protectiveness of the PCL-$TiO_2$ coating. The corrosion layer formed, characterized by SEM and EDS, as being composed of brucite, carbonates, and magnesium oxychloride in the bare and PCL coated samples contrasted with the bioactivity provided by the PCL-$TiO_2$ coating where the additional precipitation of apatites occurred. The physiological impact of the approach and data presented herein is discussed.



**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 authors acknowledge both Dr. Haiou Jin, from CANMET Materials Technology Laboratory, Dr. Shahrzad Esmaeili, also from CANMET Materials Technology Laboratory, and the University of Waterloo, from Canada, for their precious help with the alloy design.]

# P31 Hybrid biopolymer films doped by bioactive coordination polymers for antibacterial and antibiofilm applications

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The synthesis, characterization, and antibacterial properties of novel hybrid biopolymer materials doped with bioactive silver(I) coordination polymers (bioCPs) are described in this study.[1, 2] Four new bioCPs, $[Ag_4(\mu_8\text{-}H_2pma)_2]_n\cdot 4nH_2O$ (**1**), $[Ag_5(\mu_6\text{-}H_{0.5}tma)_2(H_2O)_4]_n\cdot 2nH_2O$ (**2**), $[Ag_2(\mu_6\text{-}hfa)]_n$ (**3**), and $[Ag_2(\mu_4\text{-}nda)(H_2O)_2]_n$ (**4**) were assembled from Ag sources ($AgNO_3$ or $Ag_2O$) and four different building blocks: 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 bioCP-doped biopolymer films, which were based on epoxidized soybean oil acrylate (ESOA) or potato starch (PS) as model biopolymer materials, and can be adjusted to exhibit different rates of degradability/silver release. Both bioCPs and their hybrid biopolymer films (**1**@$[ESOA]_n$, **2**@$[ESOA]_n$, **3**@$[ESOA]_n$, **4**@$[ESOA]_n$, **3**@$[PS]_n$, and **4**@$[PS]_n$) with low 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**@$[ESOA]_n$ outperformed other doped films in terms of antibacterial activity; **3**@$[PS]_n$ showed higher efficacy than **3**@$[ESOA]_n$, while **4**@$[ESOA]_n$ and **4**@$[PS]_n$ had similar antimicrobial and biofilm inhibition performance. This multidisciplinary study not only includes multiple important research areas, but it also expands an antibacterial use of bioactive coordination polymers and hybrid biopolymer materials derived from sustainable biofeedstocks such as soybean oil and potato starch.

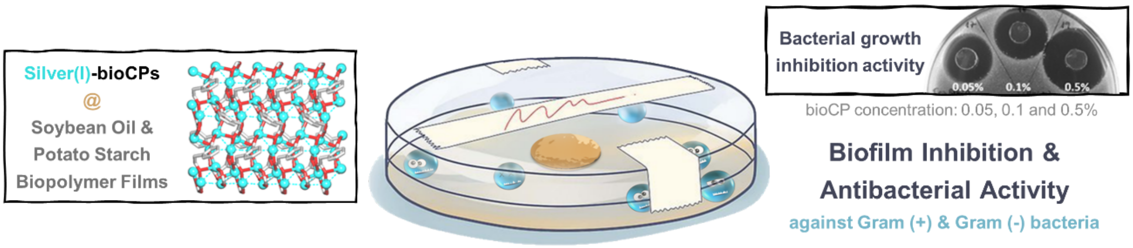

**Figure 1**. Illustration of biofilm inhibition and antibacterial activity of hybrid biopolymer materials doped with bioactive silver(I) coordination polymers.

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# P32 Fatty acids-based eutectic solvents liquid membranes for removal of sodium diclofenac 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 [1], 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 use 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.

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# P33 Particle design of active pharmaceutical ingredients using supercritical fluids

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Active pharmaceutical ingredients (API) are used in pharmaceutical products in the form of dry powders, liquid and semi-solid dispersions, which can range from nanocoloids to micro particles, depending on the dosage and the administration usage. Biopharmaceutical properties of the APIs, such as bioavailability, solubility, dissolution rate and formulations stability are directed influenced by particle size [1]. In fact, the size and the shape of the API particle will have a considerable impact in the physical properties, production processes and quality attributes of the final product. Moreover, in creams and ointments formulations for topical and ophthalmic applications, the particle size and particle size distribution can play an important role in the final product. Therefore, the production of micro and nanoparticles is an important subject for the pharmaceutical industry, as well as the process of micronization.

New approaches, such as supercritical antisolvent micronization process (SAS), are now catching the interest of the pharmaceutical industry, presenting a viable solution when compared with the traditional techniques. In fact SAS process can be considered the most suitable for the micronization of APIs, since it combines the high solvent power of SCF to dissolve the organic solvent together with the low solubility of the API in the SCF, which will be determinant for the precipitation of the pharmaceutical compounds from the organic solvent [2].

Sodium fusidate is a naturally occurring antibiotic, which has a bacteriostatic action, inhibiting bacteria from replicate, and is used to treat both topical and systemic skin and eye infections caused by *staphylococci* and other gram-positive species [3].

The objective of this work was the development of novel particles sodium fusidate with morphology and particle size suitable for its use in pharmaceutical formulations, using the SAS process. The effect of several operational parameters, such as temperature, pressure, anti-solvent/organic solvent flow-rate ratio and organic solution concentration, in the yield of the process and in the mean particle size, was evaluated using experimental design. Scanning electronic microscopy was used to determine the size and morphology of the initial and final products. On the other hand, the quality of the micronized compound was analyzed by FTIR. The crystallinity of the produced powders was also assessed through X-ray powder diffraction analysis. Nano and micro particles with morphology and particle size suitable for its use in pharmaceutic formulations were obtained.

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# P34 High temperature vapor-liquid equilibrium of alcohols+water mixtures

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Alcohols when added to gasoline can increase the octane number, reduce exhaust gas emissions, and enhance combustion. Butanol is the most similar alcohol to gasoline being therefore suitable to replace this fuel. On the other hand, butanol can be produced from fossil fuels it can also be obtained from a biomass process and thus generating a promising biofuel (bio-butanol). The general interest to produce biofuels like bio-butanol has increased due to the concerns about global warming, the restricted legislations that countries have implemented in the amount of non-renewable energy sources and the increasing price of crude oil [1]. The most used process to produce bio-butanol is by acetone-butanol-ethanol (ABE) fermentation [2]. For this process to be more efficient it is necessary a good recovery of n-butanol. To achieve this, vapor-liquid equilibrium data is the key to have a good design of a distillation column or for revamping the units that already exist [3].
In this work VLE data from several mixtures relevant to the ABE process, such as ethanol +butanol, methanol + water, and butanol + water will be compared and evaluated using the software ASPEN PLUS V11 with the purpose of retrieving new NRTL binary parameters. Several thermodynamic consistency tests will also be employed and compared, revealing its advantages and weaknesses in data evaluation.

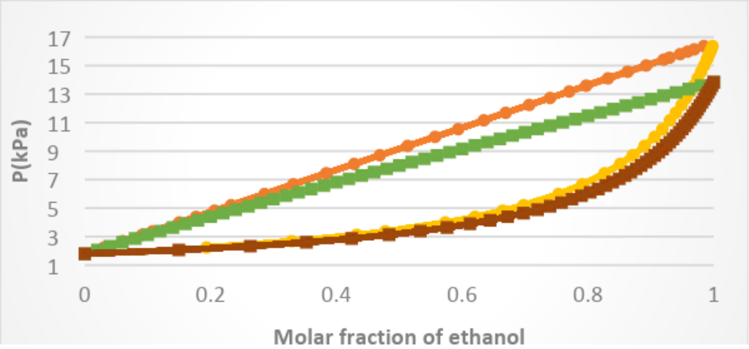

**Figure 1**. Diagram Px-y of experimental results versus NRTL model for the system ethanol-butanol at 408.15K (the circles correspond to the experimental results and the squares to the results by the nrtl model) [4].

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# P35 Study of the macroscopic properties of a binary mixture (alcohol + ionic liquid), for application in adsorption refrigeration processes

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Nowadays, sustainability is a key factor in any research or process development. Ionic liquids have been pointed as green solvents and alternatives to many organic solvents, having numerous applications, like the possibility of being used as absorbents in absorption refrigeration systems. The use of Ionic Liquids mixed with other component as a working pair in the cooling part of the process has also been pointed out as an alternative. Imidazolium based ionic liquids have been studied as alternatives [1].

The aim of this work is to provide more macroscopic data concerning mixtures of 1-ethyl-3-methylimidazolium ethyl sulfate $[C_2mim][EtSO_4]$ with an alcohol, and to contribute to ascertain the ability of the prevision models applied to these kinds of systems.

The refractive indexes of several mixtures of $\{[C_2mim][EtSO_4] + \text{1-pentanol}\}$ are herein presented, covering the entire range of composition and for temperatures T = (283.15 to 343.15) K and 0.1 MPa. Measurements were performed with an Anton Parr (Abbemat 500) refractometer, with an expanded uncertainty of $U(n) = 0.0002$, at 95% confidence level ($k = 2$), shown on **Figure 1**.

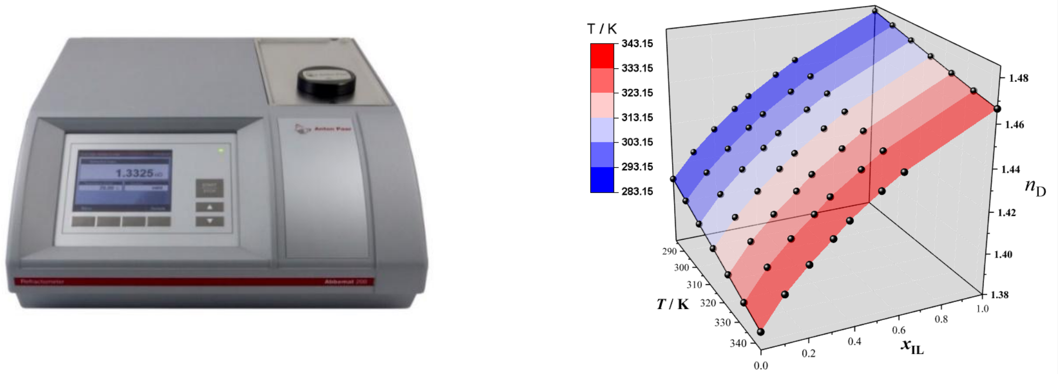

**Figure 1.** Refractive index apparatus (left) and experimental preliminary results on the refractive index of the system {1-pentanol + [C2mim][EtSO4]} (right).

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# P36 Extended lifetime of activated carbons exhausted with caffeine and paracetamol: thermal regeneration vs reactivation

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A major challenge of technologies employing adsorption onto activated carbons (ACs) is associated with extending their lifetime and the management of the spent adsorbents [1]. Nowadays, wastewater treatment is responsible for the largest amounts of exhausted granular ACs (GACs), and it is expected to growth, mainly driven by the need to remove contaminants of emergent concern, including pharmaceuticals. For this purpose, ACs adsorption and ozonation are considered consolidated technologies, with confirmed cost-efficient elimination of organic microcontaminants and toxicity in several full-scale wastewater treatment plants (WWTPs), namely in Switzerland and Germany [1]. Once the quality of the treated effluent reaches a critical point by falling below the required minimum, the loaded GAC must be replaced by fresh or regenerated GAC. Herein we address the effect of the regeneration procedure – thermal under $N_2$ flow *versus* reactivation with steam – on the effectiveness of regeneration of a commercial GAC saturated with caffeine or paracetamol to assess the influence of the adsorbate. Figure 1 reveals that the regeneration efficiency depends both on the regeneration method and the pharmaceutical compound. While in the case of caffeine the exhausted GAC is successfully regenerated under $N_2$ flow during 4 consecutive cycles (> 90% recovery of adsorption capacity), for paracetamol the regeneration with the same procedure only 50% of the adsorption capacity is recovered after the 2nd cycle. For saturation with caffeine, steam reactivation allows improving the performance in the 1st cycle but lead to a gradual decrease of regeneration efficiency and performance for consecutive cycles.

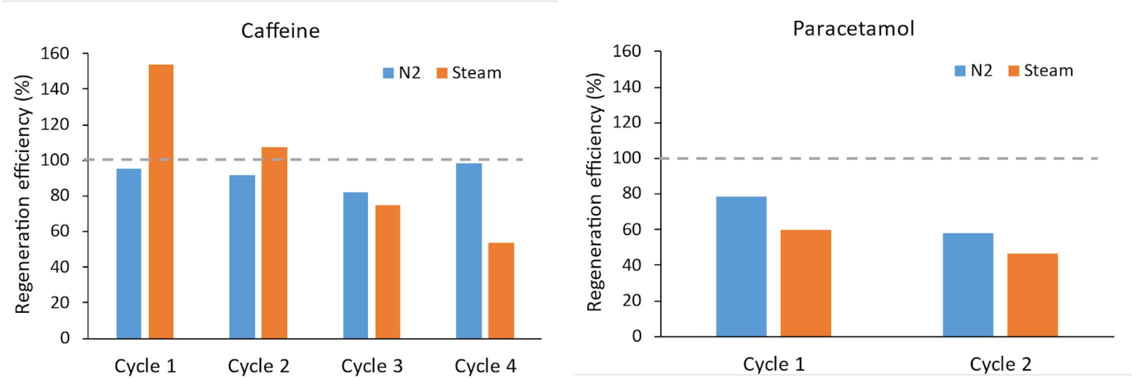

**Figure 1**. Influence of the regeneration method (thermal under $N_2$ and steam reactivation) on the regeneration efficiency of a commercial GAC exhausted with caffeine or paracetamol.

**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, and PTDC/EQU-EQU/6024/2020 (Project EMPOWER+). 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). The authors acknowledge Salmon & Cia for providing the commercial activated carbon Norit GAC830.

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# P37 PEDOT:DS as cathode material for metal-ion batteries

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Poly-[3,4-ethylenedioxythiophene] (PEDOT) is an interesting electronically conducting polymer due to its ability of being doped with different polyanions [1], making it an easily tailored material. Being also a redox active material, its high reversibility of the redox process allows for their application in battery devices [2]. PEDOT:PSS is a polymer exhibiting pseudocationic redox behavior which, allied to its intrinsic flexibility, stimulated the investigation of their use as cathode in advanced alkali metal-ion secondary batteries [3]. Dextran sulfate (DS) has been successfully used as a dopant for PEDOT [4] and the resulting polymer structure is shown in Figure 1. PEDOT:DS films were electrochemically synthesized over platinum substrate under potentiostatic and galvanostatic control. The mass transfer events resulting from the redox transformations were assessed by combining the information retrieved from data taken by cyclic voltammetry (CV), probe beam deflection (PBD) and electrochemical quartz crystal microbalance (EQCM). The characterization media consisted in acetonitrile solutions of $LiClO_4$ or $Mg(ClO_4)_2$.

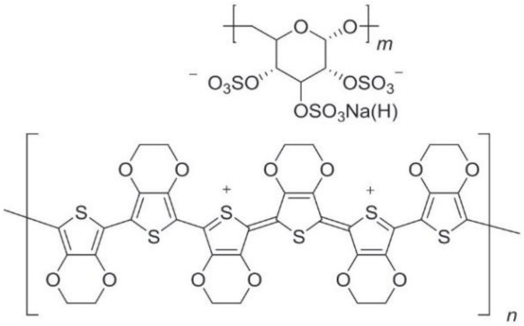

**Figure 1**. PEDOT:DS structure [4].

**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.

**References**: [1] V. Tsakova, G. Ilieva, D. Filjova; *Electrochimica Acta* **2015**, 179, 343-349. [2] N. Casado, G. Hernández, A. Veloso, S. Devaraj, D. Mecerreyes, M. Armand; *ACS Macro Letters* **2016**, 5, 59-64. [3] Z. Rahimzadeh, S. Naghib, Y. Zare, K. Rhee; *Journal of Material Science* **2020**, 55, 7575-7611. [4] D. Harman, R. Gorkin III, L. Stevens, B. Thompson, K. Wagner, B. Weng, J. Chung, M. Panhuis, G. Wallace; *Acta Biomaterialia* **2015**, 14, 33-42.

# P38 Development of $TiO_2$@PAC composites

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Adsorption onto activated carbons (ACs) has been considered one of the best available technologies to control emergent contaminants, including pharmaceutical compounds [1]. Significant improvements in AC technologies require disruptive production and regeneration processes. Thus, the need for the development of reusable ACs by combining adsorption and photocatalytic processes. $TiO_2$ is the most explored photocatalyst due to its unique properties that can be enhanced by its immobilization on powdered AC (PAC). The immobilization of $TiO_2$ on PAC ($TiO_2$@PAC composite) prevents the aggregation of $TiO_2$ nanoparticles, which will improve the contaminant/catalyst contact. Moreover, the adsorptive properties of PAC will favor the global removal process by increasing the contaminants' concentration near the semiconductor [2]. $TiO_2$@PAC composites also allow to minimize the electron/hole recombination and improve sunlight absorption. As recently proved, $TiO_2$@PAC composites, as well as PAC, can still be photocatalytic regenerated using UV radiation [3].
The $TiO_2$ nanoparticles were prepared by sol-gel method [3] and the composites were obtained by adding the desired amount of PAC during the synthesis of the $TiO_2$. Two series of composites were prepared with different $TiO_2$:PAC proportions using a commercial PAC (NS) and a lab-made material prepared by the steam activation of pine nut shell char (PNS). The materials were characterized by $N_2$ adsorption at -196 ºC, X-ray diffraction (XRD), determination of the pH at the point of zero charge ($pH_{PZC}$), Fourier transform infrared (FTIR) spectroscopy, scanning and transmission electron microscopy (SEM and TEM), and UV-Vis diffuse reflectance. The XRD diffractograms confirm that despite anatase is the dominant phase in bare $TiO_2$ and in $TiO_2$@PAC composites diffraction peaks of anatase and brookite are also detected (**Figure 1**). The $N_2$ isotherms of the composites reflect the effect of $TiO_2$:PAC proportion, and in all the cases exhibit features of both components (**Figure 2**).

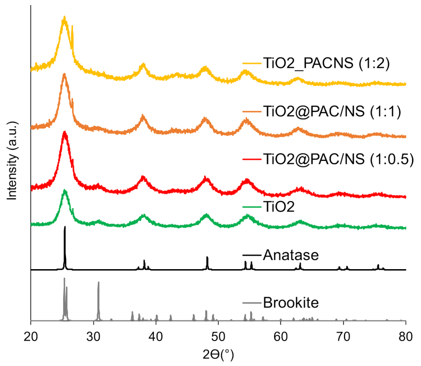

**Figure 1**. XRD diffraction of the materials.

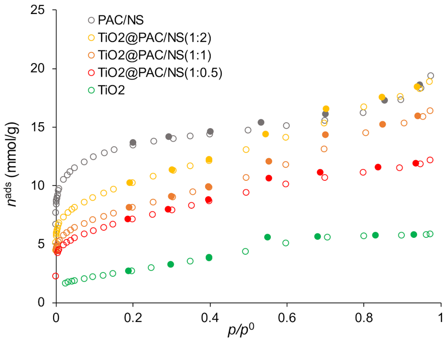

**Figure 2**. $N_2$ isotherms at -196 ºC.

**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).

**References**: [1] Mestre, A. S., Campinas, M., Viegas, R. M. C., Mesquita, E., Carvalho, A. P., & Rosa, M. J. Chapter 17 - Activated carbons in full-scale advanced wastewater treatment. In D. Giannakoudakis, L. Meili, & I. Anastopoulos (Eds.), Advanced Materials for Sustainable Environmental Remediation (pp. 433-475), Elsevier, **2022**. [2] Mestre, A. S., & Carvalho, A. P. *Molecules*, **2019**, 24, 3702. [3] Dalto, F., Kuźniarska-Biernacka, I., Pereira, C., Mesquita, E., Soares, O. S. G. P., Pereira, M. F. R., Rosa, M. J., Mestre, A. S., Carvalho, A. P., & Freire, C. *Nanomaterials*, **2021**, 11, 3016.

# P39 Perfluorinated (PFAS) pollutants in water – Interfacial properties and diffusion coefficients by molecular dynamics simulations

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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). 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.

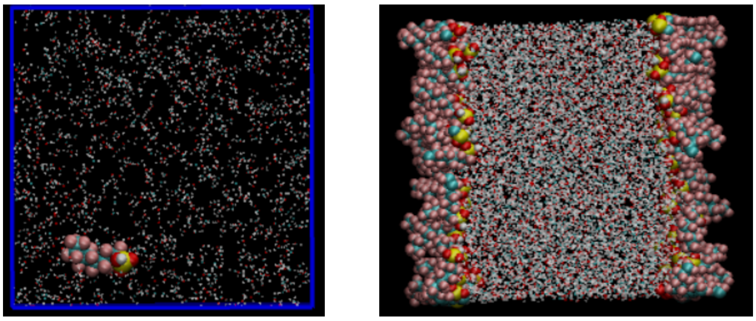

**Figure 1**. MD snaphots of typical studied systems. Left – 1 PFOS molecule at infinite dilution in water; Right – Adsorption of PFOS molecules at the liquid-vapour interface.

**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.

# P40 Interfacial properties of alkylamines – A molecular dynamics simulation study

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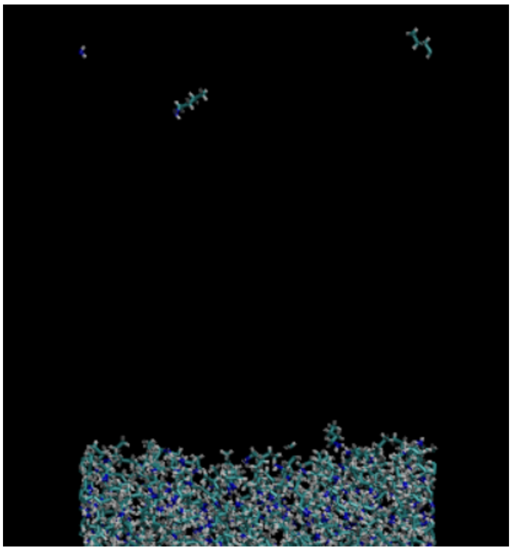
Alkylamines are surface-active compounds that are used to modulate the interfacial properties of such diverse systems as water/hydrocarbon or water/carbon dioxide emulsions, in the production of nanoparticles, micellar catalysis or in formulations of pesticides and herbicides.
In this work, molecular dynamics simulations are used to study the interfacial behaviour of primary, secondary and tertiary alkylamines. The atomistic force field employed is validated against literature experimental surface tension values for the pure amines, and the corresponding interfacial structures are obtained from the simulations and described at the molecular level. The validated molecular models are then used to obtain the structural and thermodynamic properties of relevant interfaces: the liquid/vapour interface of miscible amine/water and amine/hydrocarbon mixtures, and the liquid/liquid interface for the immiscible systems.



**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.

# P41 Location and diffusion of respiratory gases ($O_2$ and $CO_2$) and Xe in nano-segregated fluids

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Mixed hydrogenated / perfluorinated systems exhibit highly non-ideal behaviour due to the phobicity between fluorinated and hydrogenated chains. This plays a determinant role on the liquids' structure: mixtures of hydrogenated and perfluorinated amphiphiles self-assemble forming highly complex structures such as liquid crystals, gels and micellar solutions [1]. Even simpler systems such as mixtures of alkanes + perfluoroalkanes were found to be nano-segregated fluids [2]. Additionally, respiratory gases such as $O_2$ and $CO_2$ are known to be highly soluble in perfluorinated fluids and are usually considered fluorophilic. Xenon, on the other hand, is known to be "hydrogenophilic". This set of gases can thus be used to probe their location and dynamics in mixed perfluorinated/hydrogenated systems, providing important insights regarding the solvent structure.

In this work Atomistic Molecular Dynamics simulations were performed to study the location and diffusion of $O_2$, $CO_2$ and Xe dissolved in mixtures of alkanes and perfluoroalkanes and in mixtures of hydrogenated and fluorinated alcohols. Figure 1 shows a snapshot of an oxygen molecule in the bulk of an equimolar mixture of hexane + perfluorohexane. The MD results allowed to identify the nano-segregated organization of the fluid, the location of the $O_2$, $CO_2$ and Xe particles, to estimate the diffusion coefficients of $O_2$, $CO_2$ and Xe and to test the fluorophilic nature of $O_2$ and $CO_2$.

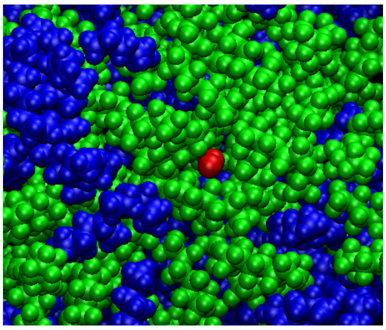

**Figure 1**. MD simulation snapshot of an oxygen molecule (red) in an equimolar mixture of hexane (blue) and perfluorohexane (green).

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SYNCat

# P42 Synthesis of unnatural conformationally constrained amino acids by cross-dehydrogenative coupling

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Metal-catalyzed cross-dehydrogenative coupling (CDC) has emerged in recent years as a powerful technique to make C–C bonds or C–X bonds (X = N, O, S, P) directly from two C–H bonds or a C–H and an X–H bond [1–3]. No prefunctionalization is required, only an oxidant to act as the terminal acceptor of the two hydrogen atoms. Coupled with homogeneous catalysis with earth abundant metals, e.g. Cu, Fe or Co, cheap and nontoxic, CDC provides environmentally friendly processes which are atom-, energy-, time- and cost-efficient. We have explored oxidative amination, i.e. C–N bond formation under oxidative conditions, as a means to obtain conformationally constrained amino acids functionalized with imides.

Since the imide group is also an important pharmacophore present in a large range of medicinally important molecules, e.g. antiepileptic, antineoplastic and anti-Parkinson drugs, amongst others (**Scheme 1a**), the new compounds are of interest for peptidomimetics, drug design and also for synthetic applications [4,5]. Scheme 1b highlights the method developed.

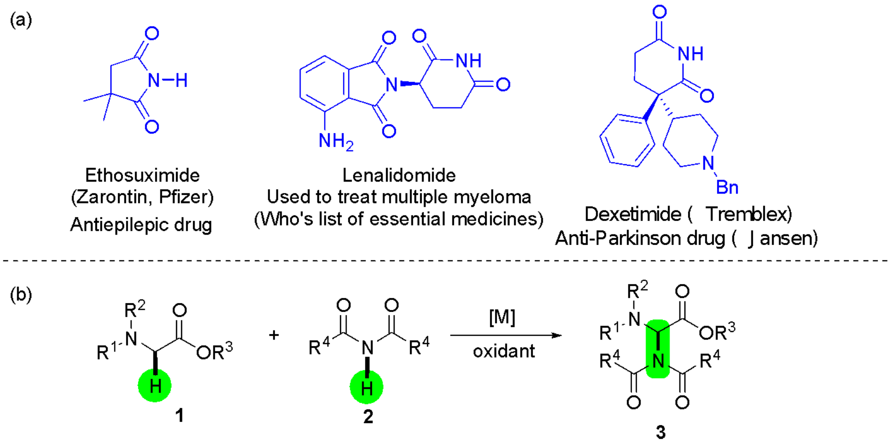

**Figure 1**. (a) Examples of pharmacologically important imides; (b) The method developed.

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# P43 Nanofluids as catalysts for sonogashira C-C coupling

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Sonogashira coupling is a widely-applied transition metal catalysed carbon–carbon bond forming reaction. However, under unconventional conditions, namely in a nanofluid where the base fluid is an ionic liquid (IL), is still understudied. [1]

In this work we present the coupling between phenylacetylene and 4-bromoanisole to afford 1-methoxy-4-(phenylethynyl)benzene (Scheme 1), using Pd(OAc)$_2$, PdCl2 or Pd/C (5% w/w) as nanocatalysts in several ionic liquids.

The use of ionic liquids as reaction media instead of harmful organic solvents is of significance towards a greener protocol. In addition, with ionic liquids based nanofluids, Sonogashira coupling reaction presents higher conversions and an easier separation and recycling of the catalyst.

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# P44 Study of photocatalytic and antimicrobial activity of new *g*-$C_3N_4$/TNW hybrid nanomaterials

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Nowadays, many thousands of products, including pharmaceuticals and personal care products (PPCPs) are used worldwide and disposed after use, in the environment. Do to their complexity, they are usually very difficult to degrade in natural conditions and, as a consequence, their accumulation in the environment is alarmingly high and it is continuously rising.

In spite of several elimination methodologies being developed to handle with this problem, the results that have been obtained were unsatisfactory, particularly in their effectiveness and efficiency. Nevertheless, advanced oxidation treatments, especially photocatalytic oxidation, have been one of the most promising solutions to the removal of PPCPs and for pollutants degradation, with titanate nanoparticles being a promising alternative as catalyst for pollutants photo-oxidation. [1]

Besides the PPCPs removal, it has been a growing interest in methodologies to allow the sterilization of surfaces in health-care related fields. There are several strategies to create a bacteria-free surface, however many of these approaches only provide a time-limit antimicrobial activity resistance to the anti-infectious agents and can release toxic elements to the environment. A challenging approach is to trigger the bacterial inactivation by employing a photocatalytic active coating. Very recently, graphitic carbon nitride (g-$C_3N_4$) has attracted considerable interest in this field. Its relatively low photocatalytic activity efficiency, it can be improved by create bandgap heterojunctions with other photocatalysts, as titanate nanoparticles and titanium dioxide ($TiO_2$). [2]

In this project, we proceeded with the synthesis of composite nanomaterials containing titanate nanowires (TNW) and $C_3N_4$ for later incorporation in thin hybrid films. After characterization, these materials were used to perform photocatalytic studies using a caffeine solution, which acted as a model pollutant. In addition, the capacity of those materials to inactivate bacteria was also evaluated and will be discussed.

**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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# P45 Catalytic synthesis of imineureas using Titanium(IV) ketimide complexes

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Ketimide ligands are mostly used as support ligands. [1] They have however also non-innocent behaviour, as previously demonstrated for Thorium complexes. [2] We have extended this behaviour to titanium chemistry. The homoleptic complex, $Ti(N{=}CPh_2)_4$ (**1**), is obtained in good yield by reacting $Ti(NMe_2)_4$ with 4 equiv. of $HN{=}CPh_2$. It catalyses the synthesis of imineureas, **2**, (Fig. 1) that are interesting compounds with application in industry and pharmacology. [3] We are also investigating the reaction of **1** with $CO_2$.

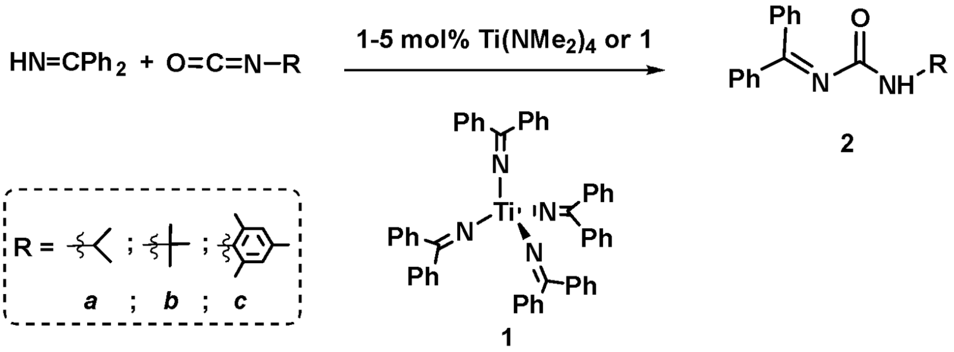

**Figure 1** Reactivity of **1** towards heteroallenes.

**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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# P46 Vinyl-addition polynorbornene from neutral iminopyrrolyl Pd(II) catalysts

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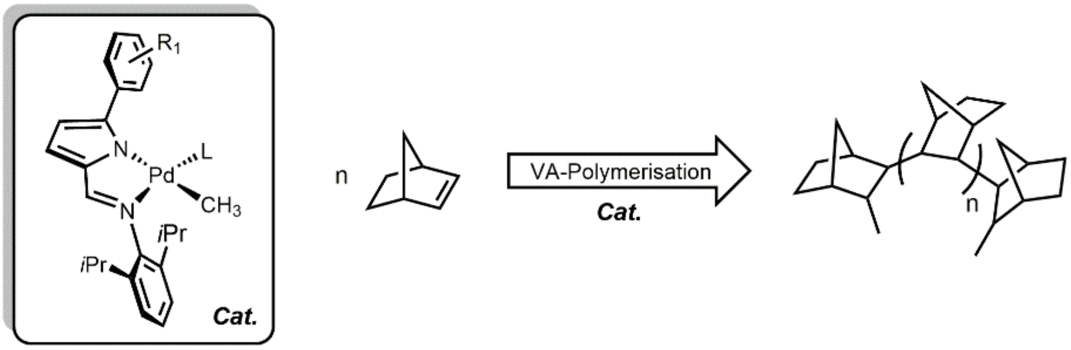
Norbornene can be polymerized via several pathways. The ROMP (ring-opening metathesis polymerization) mechanism is the best-known process, and the radical and cationic polymerizations are the less common ones. The vinyl addition (VA) polymerization mechanism is also a well-known process and has received interest in recent years.

In the VA-type mechanism, the bicyclic structure remains intact, the resulting polymers containing a saturated and rigid main chain, which confers distinct properties, such as high glass transition temperature, excellent transparency, or good chemical resistance.

Several Ni(II) and Pd(II) complexes have been explored as pre-catalysts for this type of norbornene polymerization, although they usually require the presence of aluminum activators. [1-3] In our group, α-diimine nickel complexes were developed and tested with MAO for the VA polymerization of norbornene, giving highly active catalysts. [4] Recently, we also studied aluminum-free iminopyrrolyl Ni(II) pre-catalysts that are active in the polymerization of ethylene. [5,6] In this communication, we report the synthesis of a series of iminopyrrolyl Pd(II) methyl complexes, which are active in the VA polymerization of norbornene upon activation with $B(C_6F_5)_3$ co-catalyst. Activities up to $10^6$ $g_{PNB}(mol_{Pd}.h)^{-1}$ were observed, giving rise to insoluble polynorbornenes.



L = Py, $CH_3CN$, PhCN; $R_1$ = H, 3,5-$(CH_3)_2$, 3,5-$(CF_3)_2$

**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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# P47 Preparation of hydroxylated AI metabolites

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The development of plant protection products requires the safety profile analysis of active ingredients (AIs). This includes toxicity determination of AI metabolites. A very common phase-one metabolism reaction is C-oxygenation catalyzed by cytochrome P450 enzymes[1,2]. Thus, the synthesis of oxygenated AI metabolites is of great importance to agrochemical producing companies, namely ASCENZA Agro[3], for safety evaluation purposes.

Herein, we describe the synthesis of hydroxylated aromatic metabolites of several AIs, using methods described by Tobias Ritter and co-workers[4] (**Figure 1**). This method allows the late-stage oxygenation of the aromatic positions, by generating mesylate derivatives with bis(methanesulfonyl) peroxide as an oxidant, followed by conversion to the corresponding phenols.

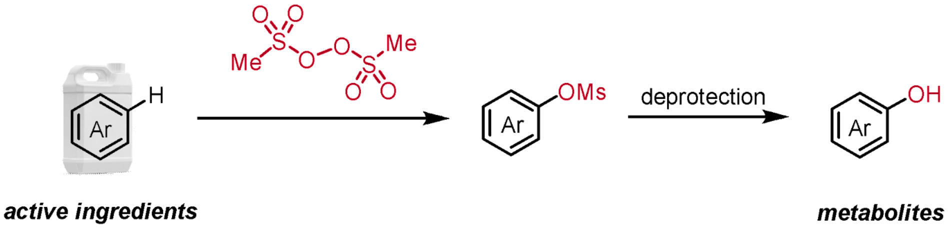

**Figure 1**. Synthetic route for the late-stage aromatic and benzylic oxygenation of AIs.

**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. Financial support from Fundação para a Ciência e a Tecnologia (FCT, UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020 and 2020/02383/CEECIND). The authors thank Dr. Ana Viana and Dr. Jorge Correia (CQE-FCUL) for assistance and equipment to perform electrolysis.

**References**: [1] Reichl, F.-X.; Schwenk, M. *Regulatory Toxicology*, 2nd ed.; Reichl, F.-X., Schwenk, M., Eds.; Springer Nature Switzerland AG: Cham, Switzerland, **2021**. [2] Guengerich, F. P. Common and uncommon cytochrome P450 reactions related to metabolism and chemical toxicity. *Chem. Res. Toxicol.* **2001**, *14* (6), 611–650. [3] https://www.ascenza.pt/. [4] Börgel, J.; Tanwar, L.; Berger, F.; Ritter, T. Late-Stage Aromatic C-H Oxygenation. *J. Am. Chem. Soc.* **2018**, *140* (47), 16026–16031.

# P48 Synthesis and structural characterization of two copper(II) 4-sulfamoylbenzoate coordination compounds

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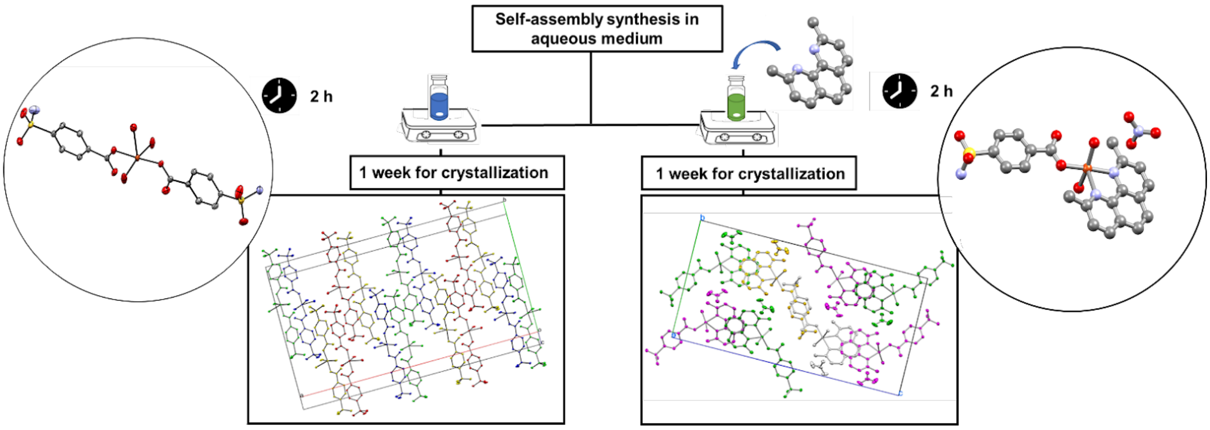
In pursuit of our general interest in the synthesis of copper(II) coordination compounds and their catalytic exploration toward mild C−H functionalization of alkanes and other substrates [1], in the present study we describe some recent synthetic strategies to obtain two novel Cu(II) complexes bearing 4-sulfamoylbenzoate ligands. Two slightly different synthetic strategies were explored, resulting in the generation of products $[Cu(psb)_2(H_2O)_3]$ (**1**) and $[Cu(psb)(neo)(H_2O)_2]NO_3$ (**2**). Both compounds were synthetized in aqueous medium by reacting $Cu^{2+}$ ions with 4-sulfamoylbenzoic acid (Hpab). While compound **1** was obtained by self-assembly at room temperature after slow addition of starting materials (Hpsb + $Cu(NO_3)_2$), the synthesis of **2** required prior treatment of $Cu(NO_3)_2$ and neocuproine (neo) before promoting the coordination with deprotonated ligand (psb−). The products were obtained as stable crystalline solids in relatively good yields and characterized by standard methods, including single-crystal X-ray diffraction (Scheme 1). The structures of **1** and **2** feature similar coordination modes of ligand (psb−) with carboxylate moieties connected by terminal monodentate bonds as well as square pyramidal coordination environments around Cu(II) centers. The use of distinct reaction and crystallization conditions is a decisive factor for the control and synthesis of these copper(II) coordination compounds. The exploration of the obtained complexes as potential homogeneous catalysts in mild oxidative functionalization of hydrocarbons is currently being investigated [1].



**Scheme 1:** Strategies for the synthesis of **1** (left) and **2** (right), including their structural representations.

**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 has also received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 860762 (CHAIR project).

**References**: [1] I. Costa, M. Kirillova, V. André, T. Fernandes, A. Kirillov; *Inorg. Chem.* **2021**, 60, 14491-14503.

# P49 Copper(II) coordination polymers vs. discrete tetracopper(II) Rings: time-dependent self-assembly, structural features and catalytic activity

Costa, Inês[A*]; Kirillova, Marina[A]; André, Vânia[A]; Fernandes, Tiago[A]; Kirillov, Alexander[A]

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The present study reports a time-dependent self-assembly formation of new copper(II) coordination compounds from an aqueous-medium reaction mixture composed from copper(II) nitrate, $H_3$bes biobuffer (*N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid), ammonium hydroxide and benzenecarboxylic acid, namely 4-methoxybenzoic (Hfmba) or 4-chlorobenzoic (Hfcba) acids. Two products were isolated from each reaction: 1D coordination polymers $[Cu_3(\mu_3\text{-}OH)_2(\mu\text{fmba})_2(\text{fmba})_2(H_2O)_2]_n$ (**1**) or $[Cu_2(\mu\text{-}OH)_2(\mu\text{-fcba})_2]_n$ (**2**) and discrete tetracopper(II) rings $[Cu_4(\mu\text{-Hbes})_3(\mu\text{-}H_2\text{bes})(\mu\text{-fmba})]\cdot 2H_2O$ (**3**) or $[Cu_4(\mu\text{-Hbes})_3(\mu\text{-}H_2\text{bes})(\mu\text{-fcba})]\cdot 4H_2O$ (**4**), respectively. The compounds were obtained as stable crystalline solids in relatively good yields and characterized by standard methods, including single-crystal X-ray diffraction.[1] The structures of **1** and **2** feature distinct types of metal-organic chains driven by the $\mu_3$- or $\mu$-$OH^-$ ligands along with the μ-benzenecarboxylate linkers. The structures of **3** and **4** disclose the chair-like $Cu_4$ rings assembled from four μ-bridging and chelating aminoalcoholate ligands along with μ-benzenecarboxylate moieties. To evaluate the catalytic activity of **1**−**4**, two model reactions were explored, namely (a) the mild oxidation of saturated hydrocarbons with hydrogen peroxide to form alcohols and ketones, and (b) the mild carboxylation of alkanes with carbon monoxide, water and peroxodisulfate oxidant to generate carboxylic acids. Apart from notable catalytic activity and widening the family of Cu-based catalytic systems, this study showcases a novel time-dependent synthetic strategy for the self-assembly of two different Cu(II) coordination compounds from the same reaction mixture.

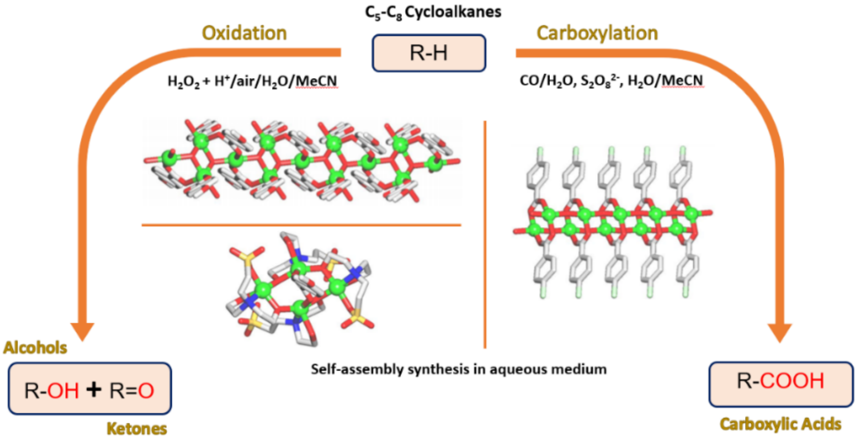

**Figure 1**. Model Cu-catalyzed hydrocarbon oxidation and carboxylation reactions.

**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 work was also supported by the FCT (projects PD/BD/150418/2019, PTDC/QUI-QIN/3898/2020).

**Reference**: [1] Costa, I.F.M.; Kirillova, M.V.; André, V.; Fernandes, T.A.; Kirillov, A.M.; *Inorg. Chem.* **2021**, 60, 14491-14503.

# P50 Catalysis by metal oxide-supported gold nanoparticles: Azide-alkyne cycloaddition reaction for triazole synthesis

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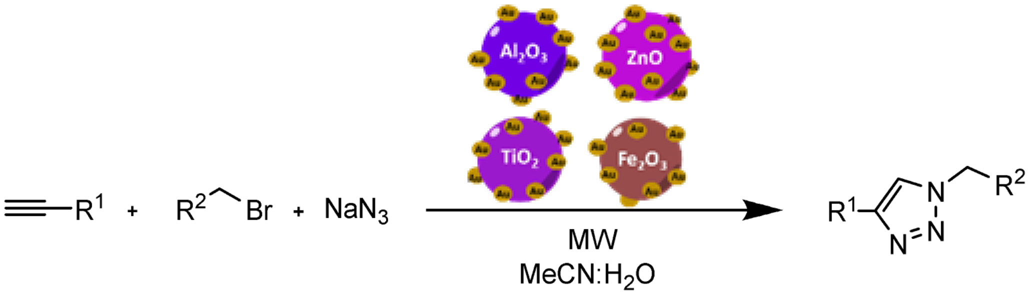
In association with the continuous research interest on the development of effective catalysts for the azide-alkyne cycloaddition (AAC) [1] reaction beyond copper-based catalysts [2,3], herein, we report the use of Au nanoparticles (Au NPs) supported on various metal oxides (viz., $Al_2O_3$, $Fe_2O_3$, $TiO_2$ and ZnO) as heterogeneous catalysts. The supported Au NPs with metal loadings of 0.7-1.6% (w/w relative to the support) were able to obtain 1,4-disubstituted 1,2,3-traizoles in moderate yields up to 79% after 15 minutes under microwave irradiation through a one-pot, three-component system.



**Scheme 1**. Synthesis of triazoles catalyzed by Au NPs on different metal oxide supports under MW irradiation.

**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. FCT/MCTES (UIDB/50006/2020 and UIDP/50006) from Associate Laboratory for Green Chemistry-LAQV. I.L.L. for her CATSUS PhD grant PD/BD/135555/2018.

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# P51 New hybrid titanate nanotubular materials with UV-protective properties

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Due to climate change and environmental degradation climate, the raising up of UV radiation that reaches Earth, is nowadays a global problem that urgently needs to be addressed not to compromise (more) future generations. Therefore, it is urgent to search for new materials, with improved UV-blocking properties, suitable for use as shields/protectors.

In this work it is intended to explore the use of new hybrid materials of titanate nanotubes (TNTs), as a protective barrier to suppress the adverse effects caused by photo-oxidation in organic matter, when exposed to UV-vis radiation.

TNTs is a biocompatible nanomaterial that have similar structure and photocatalytic properties to $TiO_2$. Moreover, TNTs have higher surface area, enhanced adsorption/intercalation ability and lower photo-generated charge carriers' recombination rate. After use as photo-protectors, their discharge into the environment should not have negative impact since TNTs have been demonstrated photocatalytic ability for pollutants degradation. It has been investigated by us for emergent pollutants degradation [1].

In this work, TNTs particles were prepared and afterwards modified using lignin, a low-cost sub-product of wood transformation industry. After characterization by FTIR, XRD and DRS, the analysis of the photocatalytic performance of these materials under visible radiation, was evaluated using caffeine as model organic molecule. The obtained results will be presented and discussed.

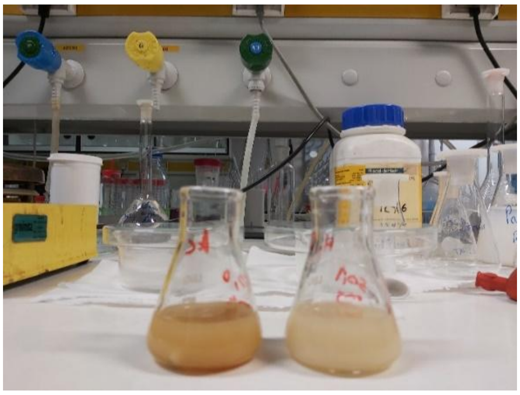

**Figure 1**. Titanate nanotubes after treatment with lignin solutions.

**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.

**References**: [1] B. Barrocas, T.J. Entradas, C.D. Nunes, O.C. Monteiro; "Titanate nanofibers sensitized with ZnS and $Ag_2S$ nanoparticles as novel photocatalysts for phenol removal", *Journal of Materials Science* 47 (**2017**) 709-720.

# P52 Hydrogenation of aldehydes and ketones with a new ruthenium complex

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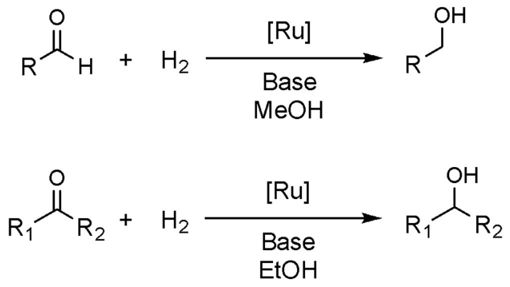
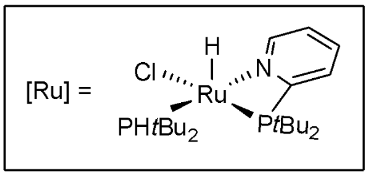
The hydrogenation of aldehydes and ketones are very important reactions in synthetic chemistry, having industrial relevance in the synthesis of alcohols. [1,2] We have recently developed a new Ruthenium (II) hydride complex that catalyzes the hydrogenation of these substrates. We report here the formation of several benzylic and alkylic alcohols obtained by the reduction of the corresponding aldehydes, as well as the hydrogenation of several ketones.





**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).

**References**: [1] Nicholas B. Johnson, Ian C. Lennon, Paul H. Moran, James A. Ramsden; *Acc. Chem. Res.* **2007**, 40, 1291–1299. [2] Lionel A. Saudan; *Acc. Chem. Res.* **2007**, 40, 1309–1319.

# P53 Luminescent Ce(III) bis(aryloxide) cyclam complexes

Maria, Leonor[A]*; Paulo, Pedro M. R.[A]; Carvalho, M. Fernanda. N. N.[A]; Marçalo, Joaquim[A]; Santos, Isabel. C.[B]; Oliveira, Sandrina[A]; Bandeira, Nuno A. G.[C]

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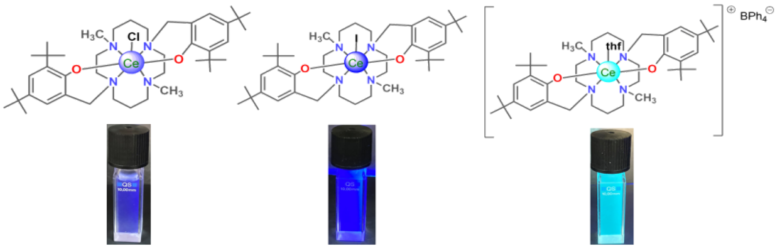
Cerium is the most abundant of the rare earth elements and is one of the most inexpensive. It displays low-to-moderate toxicity and plays an important role in organic synthesis [1]. Although $Ce^{3+}$ ions exhibit intrinsic 4f→5d optical absorption transitions, the corresponding luminescence has not typically been observed in molecular Ce(III) compounds, likely due to rapid deactivation of their excited states by non-radiative relaxation pathways. Nevertheless, the number of reported luminescent $Ce^{3+}$ complexes has increased in the last years, with a large variation in the luminescence properties, e.g. the emission wavelength could be adjusted by varying the coordination environment [2,3]. Some of these complexes have demonstrated to be photocatalytically active [3], and others are expected to be more stable in OLEDs since their excited-state lifetimes are generally in the order of nanoseconds [4].
Herein, we will report our recent results on synthesis and characterization of Ce(III) complexes supported by a bis(aryloxide) cyclam ligand. The Ce(III) compounds exhibit, in tetrahydrofuran, broad absorption bands in the UV region and are violet or blue emitters under UV irradiation. The photoluminescence properties of the Ce(III) complexes $[Ce\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}X]$ (X = Cl (**1**), I (**2**)) and $[Ce\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(thf)][BPh_4]$ (**3**) were studied via emission spectra and decays, which afforded the emission quantum yield of these samples. In an effort to identify the electronic transitions in **1**, **2** and **3**, time-dependent density functional theory (TD-DFT) calculations are being conducted. In order to evaluate the redox properties of the complexes, their electrochemical behavior was studied by cyclic voltammetry in thf and preliminary results will be also presented.



**(1)** **(2)** **(3)**

**Figure 1**. Thf solutions of **1**, **2** and **3** complexes in quartz cells under 365 nm UV irradiation.

**Acknowledgments:** Centro de Química Estrutural (CQE), C$^2$TN and BioISI are Research Units funded by Fundação para a Ciência e Tecnologia through projects UIDB/00100/2020 (CQE) and UIDP/00100/2020 (CQE), UIDB/04349/2020 (C$^2$TN) and UIDB/04046/2020 (BioISI). Institute of Molecular Sciences (IMS) is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

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# P54 Reconciling antagonistic interpretations of solvent effects in the reactivity of tertiary alkyl halides

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The study of solvent effects in the reactivity of tertiary alkyl halides has provided intense debates centered on several issues and controversies, namely: the quest for the best similarity model or multiparametric equation [1], the discussion on the presence or absence of nucleophilic assistance/solvation in these systems [2], or the reasoning on how to quantify solvent effects [3]. One of the most puzzling questions has to do, undoubtedly, with the understanding of log $k_{\text{2-chloro-2-methylbutane}}$ vs. log $k_{\text{1-chloro-adamantane}}$ plots (*t*BuCl vs. AdCl – **fig. 1**), usually called Grunwald-Winstein (G-W) plots. The observed kinetic deviations for fluorinated hydroxylic solvents and their mixtures compared to non-fluorinated aqueous media have been interpreted differently: for some authors, it has been taken as an influence of nucleophilic solvent assistance (NSA) in *t*BuCl [4]; for others, it has been perceived as a lesser influence of electrophilic solvent assistance (ESA) exerted on *t*BuCl (compared to AdCl) [5].

In the present work we put forward a set of arguments which demonstrate that both rationales are indeed depicted in the G-W plots. We show that: *i*) the kinetic deviations observed in the G-W plots pale into insignificance when a set of pure solvents ranging from acetone to water is analyzed; *ii*) a small NSA can still be quantified through the displacement of log $k_{water}$ from the line formed by the other pure solvents; *iii*) the slope of the referred line, mostly quantifies the lower influence of ESA in *t*BuCl by comparison with AdCl.

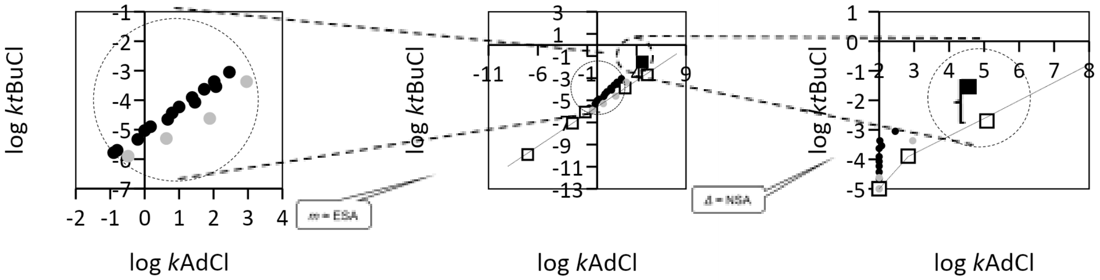

**Figure 1**. log $k_{tBuCl}$ vs. log $k_{AdCl}$: non-fluorinated aqueous media (●); fluorinated hydroxylic solvents and their mixtures (●); water (■); other pure solvents (□).

**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.

**References**: [1] L. Moreira, M. Reis, R. Elvas-Leitão, M.H. Abraham, F. Martins; *J. Mol. Liquids* **2019**, 291, 111244. [2] J.P. Richard, M.M. Toteva, T.L. Amyes; *Org. Lett.* **2001**, 3, 2225–2228. [3] M.H. Abraham, F. Martins, R. Elvas-Leitão, L. Moreira; *Phys. Chem. Chem. Phys.* **2021**, 23, 3311-3320. [4] T.W. Bentley, G.E. Carter; *J. Am. Chem. Soc.* **1982**, 104, (21), 5741-5747. [5] J.J. Gajewski; *J. Am. Chem. Soc.* **2001**, 123, (44), 10877-10883.

# P55 Solvent-free oxidation of 1-phenylethanol to acetophenone catalyzed by $Cu(NO_3)_2 \cdot 2.5H_2O$ – a fine laboratory experiment for undergraduate students

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The work describes a microwave-assisted and solvent-free protocol for 1-phenylethanol oxidation to acetophenone using the inexpensive $Cu(NO_3)_2 \cdot 2.5H_2O$ salt as catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant.
This laboratory experiment, directed to undergraduate students in a class room environment, shows that a very simple system, using a readily available catalyst, can be applied for the conversion of a hydroxyl functional group into a carbonyl group. Additionally, it reveals how green chemistry can be applied on synthesis, by using microwave heating source to reduce reaction times and energy requirements, restraining the use of solvents, and eliminating purification steps. Microwave-assisted organic synthesis is a fast growing research area and it offers opportunities for new reactions which are otherwise not feasible *via* conventional heating methods. The students are confronted to the notion of a one-pot synthesis for a typical reaction, along the characterization of the product by $^1H$ NMR spectroscopy. All the practical aspects of learning are evaluated during the work, followed by a theoretical review on the reaction mechanism for alcohol oxidation promoted by a copper salt. [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. L. Frija express gratitude to FCT for the work contract no. IST-ID/115/2018.

**References**: [1] Luís M. T. Frija*, Bruno G. M. Rocha and Armando J. L. Pombeiro; Microwave-Assisted Oxidation of 1-Phenylethanol to Acetophenone Catalyzed by $Cu(NO_3)_2 \cdot 2.5H_2O$ under Solvent-Free Conditions, *J. Chem. Education* **2022** (*in prep.*).

# P56 Addition of a phenyl group to tertiary alkyl halides: solvent and structural effects in reactivity

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The Grunwald-Winstein (G-W) equation was one of the first developed methodologies to study solvent effects in the reactivity of tertiary alkyl halides. Originally intended to measure the effect of solvent's ionizing power [1], it was later modified to include a parameter designed to quantify the influence of nucleophilic solvent assistance (NSA) [2]. Additionally, a term named as "aromatic ring parameter" (*I*) was also incorporated to measure the degree of charge delocalization [3]. In a previous work, we have studied the influence of carbon-carbon multiple bonds on the heterolysis reactions of several tertiary alkyl halides and claimed that *I* was not a pure parameter [4], suggesting that caution should be taken in its use.

In the present work, we study substrates (1) to (6) – **fig.1a** – and use an alternative approach to interpret log *k vs*. $Y_X$ G-W plots as a whole and address solvent and structural effects in reactivity, based on the slope and the intercept of the line that goes through non-aqueous solvents. We show that: *i*) the *I* term is not an efficient parameter to quantify solvent effects; *ii*) substrates (3), (4) and (6) exhibit a small NSA influence; *iii*) substrates (1), (2) and (5) show a similar response to solvent effects, as well as substrates (4) and (6); *iv*) the charge resonance stabilization provided by the phenyl group on substrate (1) clearly increases its intrinsic reactivity (lowering $\Delta^{\neq}G$), whereas the electron-withdrawing effect of the methyl phenyl group on substrate (4) decreases its intrinsic reactivity (increasing $\Delta^{\neq}G$) – **fig. 1b**.

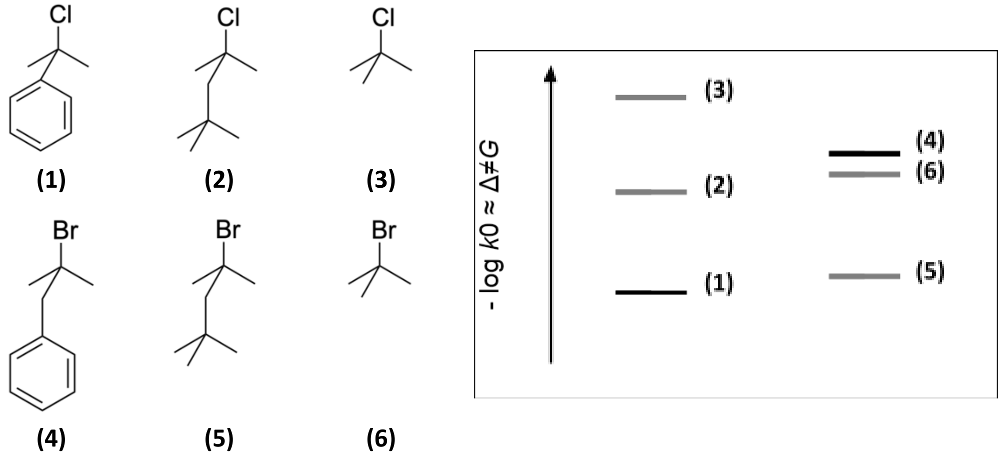

**Figure 1**. (a) substrates (1) to (6); (b) - log $k_0 \approx \Delta^{\neq}G$ for substrates (1) to (6).

**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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# P57 Indium-Cerium bimetallic oxides as catalysts for the methanation of $CO_2$

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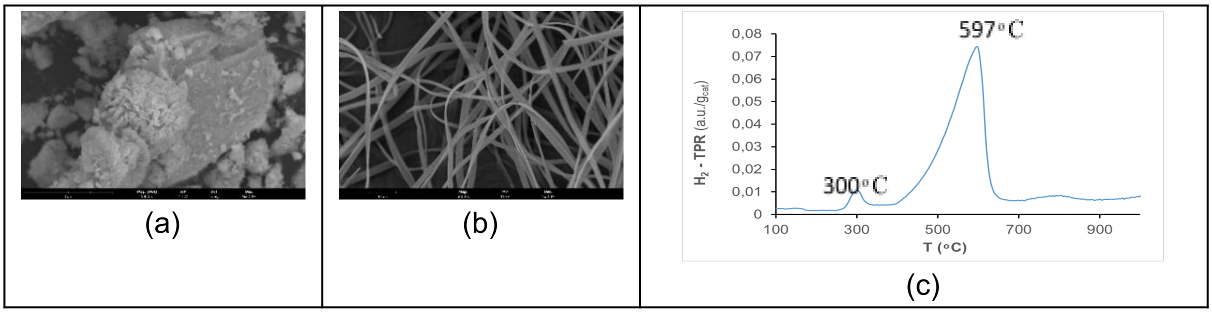
One of the most important research goals around the world is the reduction and valorization of gaseous pollutants like carbon dioxide. $CO_2$ mitigation and conversion into value-added products, such as hydrocarbons and alcohols, are two key methods that are still being developed. [1] The hydrogenation of $CO_2$ using renewable $H_2$ is currently under intensive study aiming the production of methane, higher hydrocarbons or methanol, that can be used as biofuels in several energy applications, industry, and mobility.[2]

Metal oxides such as $In_2O_3$ and $CeO_2$ have caught attention of researchers as heterogeneous catalysts or catalysts additives, namely for the activation of carbon dioxide.[3]

The main objectives of this work were the preparation of bimetallic oxides of the type $3In_2O_3{\cdot}2CeO_2$, $In_2O_3{\cdot}2CeO_2$, and $In_2O_3{\cdot}6CeO_2$, and $In_2O_3$ and $CeO_2$ using two methods (epoxide addition and electrospinning technique) in order to obtain different morphologies (Figure 1) and their evaluation as catalysts for the hydrogenation of $CO_2$. The catalysts surface morphology and composition were analyzed by SEM/EDS and whereas the epoxide addition method allows the obtention of nanoparticles with a spongy look, nanofibers were obtained using the electrospinning technique. The bimetallic oxides were also characterized by BET (measurement of their specific surface areas) and $H_2$-TPR (Temperature programmed reduction) aiming the determination of its redox properties under hydrogen. The catalytic tests were carried out in a U-shaped quartz reactor and the catalysts activity evaluated at atmospheric pressure under different conditions of temperature and volumetric flow rates of $CO_2$ (different GHSV, gas hourly space velocity in $mLCO_2/g_{cat}.h$). Preliminary results show that $3In_2O_3{\cdot}2CeO_2$ fibers have the biggest specific surface area, 29,4 $m^2/g$, and that $In_2O_3{\cdot}6CeO_2$ nanoparticles have the best reducibility. Moreover, $In_2O_3{\cdot}2CeO_2$ proved to be active and selective for the methanation of $CO_2$ at relatively low temperatures (<350 ºC).



(a)

(b)

(c)

**Figure 1.** SEM images obtained after the two types of pre,paration techniques: a) epoxide addition method, b) electrospinning technique, c) representative $H_2$-TPR profile for all the catalysts.

**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.

**References**: [1] Branco, J., Ferreira, A., Vieira, F. and Martinho, J.; Energy & Fuels **2021**, vol, 35, pp. 6725-6737. [2] Stangeland, K., Kalai, D., Li, H. and Yu, Z.; *Energy Procedia* **2017**, vol, 105, pp. 2022-2027. [3] Shen, C., Bao, Q., Xue, W., Sun, K.; *Journal of Energy Chemistry* **2022** vol 65, pp.623-629.

# P58 Solution enthalpies of API's in the ternary mixture water–choline chloride–ethylene glycol

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Solution enthalpies of active pharmaceutical ingredients (APIs) in various media are important thermochemical properties but they are seldom found in the literature. On the other hand, deep eutectic solvents (DES), a new class of solvents that has emerged in recent years, often present rather high viscosities that hamper further applications, and one way to overcome this problem is to use water as co-solvent.

Following previous works [1], we present herein the solution enthalpies, at 298.15 K, of three different API solutes - ibuprofen, paracetamol and isoniazid (**Figure 1**) - in the ternary DES mixture water-choline chloride-ethylene glycol. The behavior of the various API's in the referred mixture and the quantification and rationalization of the enthalpy values in the ternary fractions is thoroughly discussed.

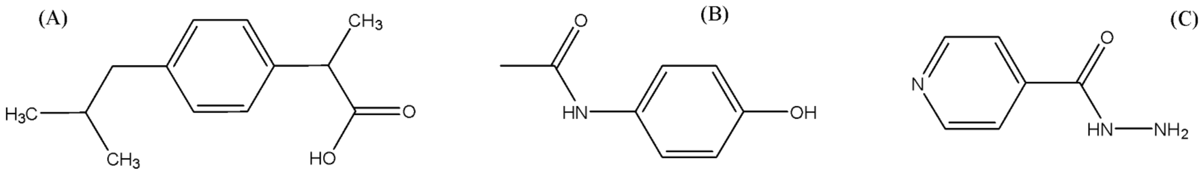

**Figure 1**. APIs used (A) – Ibuprofen, (B) – Paracetamol, (C) – Isoniazid.

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

**References**: [1] N. Nunes, M. Reis, L. Moreira, R. E. Leitão, F. Martins; *Thermochim. Acta* **2013**, 574, 85-87.

# P59 Biological properties of phenolic extracts from *Pistacia lentiscus* fruit and inhibition of acetylcholinesterase activities

Rabha Ayad[A,C*]; Nadia Amessis-Ouchemoukh[A]; Salim Ouchemoukh[B]; Dyhia Sadou[A]; Nawel Guenaoui[B] ;Rita Pacheco[C]; Maria Eduarda Araújo[C]

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*Pistacia lentiscus* L. belonging to the family Anacardiaceae, is one of the spontaneous plants most used in Algeria. The aim of this work was to evaluate quantitative and qualitatively the phytochemical composition of *Pistacia lentiscus* berries during the ripening stages. Inhibition of acetylcholinesterase activity was determined. The antioxidant activity was determined by the reducing power, FRAP, CUPRAC, CAT, DPPH, ABTS, and Ferrozine assays. ATR-FTIR spectra of the extracts was acquired at a spectral resolution of 4 cm$^{-1}$ in the range of 4000 to 650 cm-1 with 124.scans at room temperature. The samples were placed on ZnSe crystal plate. OMNIC software was used as an interface between the computer and the spectrophotometer. Experimental data will be presented.

The phytochemical screening showed that the berries were rich in anthocyanins, hydrolizable tannins and flavonoids with a variable intensity according to the stage of maturity of the studied fruit with moreover, an absence of alkaloids. Red berries showed a preponderance in polyphenols and flavonoids contents while black berries were found to be rich in carotenoids and vitamin C. The antioxidant capacities exerted by the berries were closely related to the stage of ripening and the content of phenolic compounds. FTIR spectra shows thar read berries can be a source of ellagitannins. *P. lentiscus* berries represents a reservoir of very interesting natural bioactive substances that could be used as ingredients in many fields.

**Keywords:** *Pistacia lentiscus* L. Ripening stage. Phytochemical composition. Antioxidant activities. FTIR-ATR. Acetylcholinesterase.

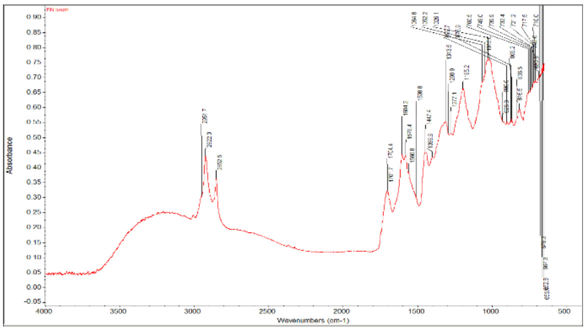

**Figure 1.** ATR-FTIR spectra of the crude extracts of Pistacia lentiscus black fruits.

**Acknowledgments:** Rabha Ayad acknowledge the Algerian Ministry of High Education and Scientific Research for sponsoring this work and Maria Eduarda Araújo acknowledge FCT financial support through the project LA/P/0056//2022.

# P60 Characterization of phenolic extracts from *Pistacia lentiscus* fruits and biological properties at several ripening stages

Rabha Ayad[A,C*]; Nadia Amessis-Ouchemoukh[A]; Salim Ouchemoukh[B]; Dyhia Sadou[A]; Nawel Guenaoui[B] ; Rita Pacheco[C,D] and Maria Eduarda Araújo[C]

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*Pistacia lentiscus* L. belongs to the family *Anacardiaceae* and is one of the spontaneous plants widely used in Algeria in local traditional medicine [1; 2]. The aim of this work was to evaluate the phytochemical composition of *Pistacia lentiscus* berries during its ripening stages, both quantitative and qualitatively. Red and black berries residues fibrous material after oil extraction were used to prepare several extracts and these were characterized. The antioxidant activity was determined by the reducing power of DPPH, ABTS, FRAP, CUPRAC, CAT, and Ferrozine assays. ATR-FTIR spectra of the extracts were acquired Extracts inhibition of acetylcholinesterase (AChE) activity were determined. Experimental data will be presented.

The phytochemical screening showed that the extracts were rich in phenolic compounds, such as anthocyanins, hydrolysable tannins and flavonoids with variable intensities and, according to the stage of maturity of the studied fruit, all the extracts have shown an absence of alkaloids. Extract from the red berries showed a preponderance in polyphenols and flavonoids contents, while black berries were found to be rich in carotenoids and vitamin C. Both the antioxidant capacities and capacity to inhibit AChE exhibited by the extracts were seen to be associated to the stage of ripening of the berries and the content in phenolic compounds. FTIR spectra showed that extract from red berries can be a source of ellagitannins. *P. lentiscus* berries residues represents a reservoir of very interesting natural bioactive compounds that could be used as ingredients in many fields.

**Keywords:** *Pistacia lentiscus* L. Ripening stage. Phytochemical composition. Antioxidant activities. FTIR-ATR. Acetylcholinesterase.

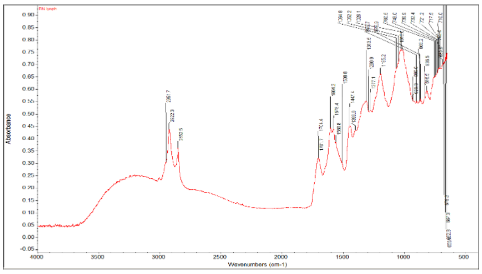

**Figure 1.** ATR-FTIR spectra in the range of 4000 to 650 cm$^{-1}$ of the residue extracts of *Pistacia lentiscus* black fruits. A ZnSe crystal plate was used and 124 scans were acquired at room temperature at a spectral resolution of 4 cm$^{-1}$. OMNIC software was used to analyse the results

**Acknowledgments:** Rabha Aayad acknowledge the Algerian Ministry of High Education and Scientific Research for sponsoring this work and Maria Eduarda Araújo acknowledge FCT financial support through the project LA/P/0056//2022.

**References**: [1] Mezni, F., Maaroufi, A., Msallem, M., Boussaid, M., Khouja, M. L., & Khaldi, A. (**2012**). Fatty acid composition, antioxidant and antibacterial activities of Pistacia lentiscus L. fruit oils. *Journal of Medicinal Plants Research*, 6(39), 5266-5271. [2] Botineau, M. (**2015**). Guide des plantes à fruits charnus comestibles et toxiques. Paris : Lavoisier, 174p.

# P61 Homogeneous electroreduction of $CO_2$: Fe(III) salphen as catalysts

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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 $CO_2$ 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 (CO and $H_2$) or directly to liquid fuels (methanol and/or methane).

The electroconversion 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.

The Fe(III) complexes are known for being good catalysts and the synthesis with salphen (N,N'-bis(salicyldene)-1,2-phenylenediamine) ligands is easy and with high yields. Therefore, the synthesis and characterisation of a mononuclear Fe(III) saphen complex is reported. Cyclic voltammetry, spectroelectrochemical and electrocatalyst studies of the complex are also investigated to be used as catalysts.

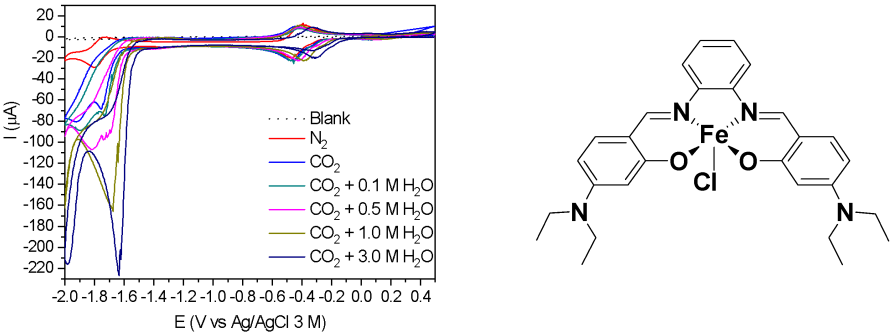

**Figure 1**. Cyclic voltammograms of complex (1 mM) in $CH_3CN$ under $N_2$ or $CO_2$ saturated solutions. Addition of different amounts of $H_2O$ to the $CO_2$ saturated solutions.

**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. We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021. 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). S.R. acknowledges FTC for financial support (2020.02134.CEECIND).

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# P62 Counter-ion effect in the magnetic properties of Fe(III) X-Br-SalEen complexes

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In the last few decades, materials and complexes exhibiting spin crossover (SCO) have sparked quite a bit of interest, due to their possible applications as memory devices, sensors and/or switches, utilizing their magnetic, optical, or luminescent responses to temperature, pressure, or even both [1].

However, designing these complexes is still a great challenge [2]. As such, in this study, we have varied the position of a -Br substituent on the aromatic ring portion of our **SalEen** ligand, formed **Fe(III)** complexes and used different counter ions for each -Br compound, with hopes of finding a correlation between ligands and the magnetic behaviour. To achieve this, the ligand was synthesized by reacting the starting X-Br-salicylaldehyde with N-ethylethylenediamine, then adding different salts, in combination with $FeCl_2$, to obtain the various counter-ions ($ClO_4^-$, $BF_4^-$, $PF_6^-$, $NO_3^-$, $Cl^-$, $OTf^-$, $I^-$ and $BPh_4^-$).

The complexes have been characterized by SQUID magnetometry, FTIR and UV-vis spectroscopy. The compounds have shown a wide range of magnetic profiles, some displaying hysteresis loops and others gradual and complete SCO (**Figure 1**).

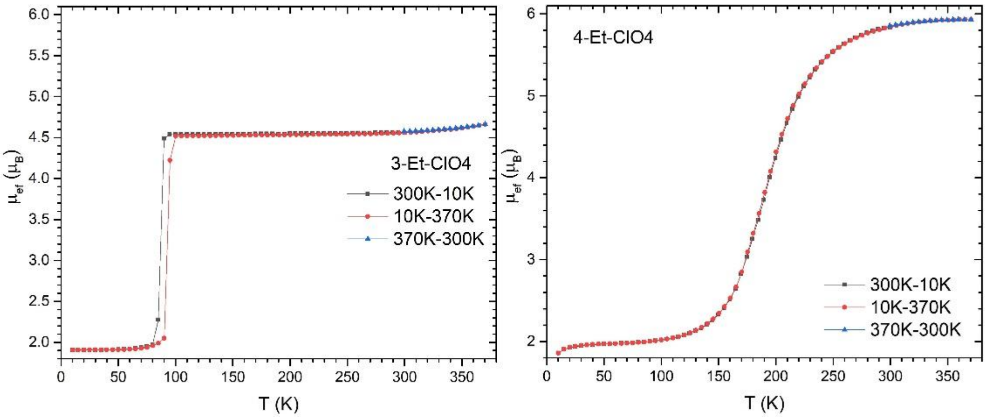

**Figure 1**. Comparison between X=3 and X=4's magnetic profiles for **[Fe(X-Br-SalEen)$_2$]ClO$_4$**.

**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. We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021.
P.N.M. acknowledges FTC for financial support (CEECIND/00509/2017).

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# P63 Iminopyrrolyl titanium preactalyst for the intermolecular hydroamination of alkynes

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Following our recent work on bulky 2-iminopyrroles (HL) and the application of their deprotonated species (L-) as bidentate ligands in late-transition metal complexes, [1-3] we report the synthesis of a new family of sterically congested and electronically unsaturated mono(5-aryl-2-iminopyrrolyl)tris(dimethylamido)titanium(IV) complexes. The resulting amido complexes [Ti(L)($NMe_2$)$_3$] were tested in the cyclohydroamination of aminoalkenes, revealing to be effective precatalysts for this transformation. The most active precatalyst was determined and further applied in the hydroamination of alkynes with primary amines for the synthesis of imines. The hydroamination of both terminal and internal alkynes was performed with alkyl and aryl amines using complex **C1** as precatalyst. Among the terminal alkynes successfully tested, precatalyst **C1** catalyzed the regioselective hydroamination of 3-phenyl-1-propyne and 1-hexyne with alkyl amines to give the anti-Markovnikov products.

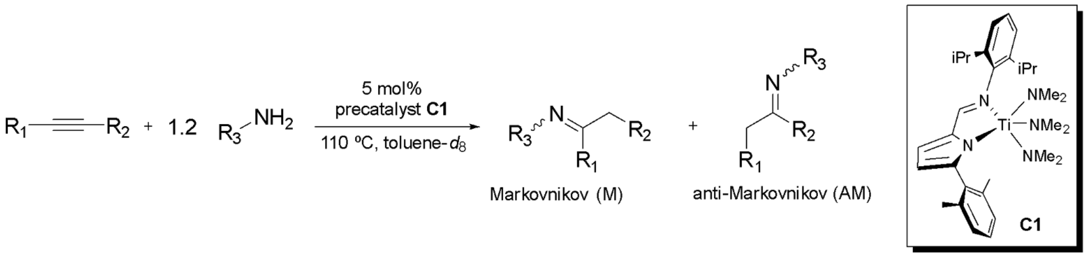

**Figure 1**.Catalytic Intermolecular Hydroamination Reaction Catalyzed by Complex **C1.**

The activity of **C1** was further explored with 1-hexyne and several different amines. Anilines containing *para*-substituents led to fast reactions with very good yields, revealing good functional group tolerance and favouring the Markovnikov product. Conversely, when anilines with *ortho*-substituents were tested, no hydroamination products were observed.
The more challenging hydroamination of symmetrical internal alkynes (diphenylacetylene and 3-hexyne) was extremely time-consuming, generating poor yields. However, reactions of the unsymmetrical 1-phenyl-1-propyne with aryl and alkyl amines are more favorable due to the presence of the aryl group attached to the C-C bond, leading preferentially to the anti-Markovnikov regioisomer. These preliminary results suggest that the sterically bulky precatalyst **C1** does not accommodate well bulky substrates, either amines or alkynes.

**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. R.A.R. is greatly acknowledge for the fellowship PD/BD/135533/2018 under the CATSUS PhD Programme.

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# P64 Gas-phase reactions of anionic Gold(I) complexes with nitrogen oxides ($NO_x$)

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Gas-phase reactions of transition metal ions with small molecules have been extensively studied [1] because they are good models for understanding the fundamentals of catalytic processes [2]. In this work, gas-phase ion chemistry studies were performed using quadrupole ion trap (QIT) mass spectrometry (MS) with electrospray ionization (ESI).
We previously prepared in the gas phase anionic Au(I) bis(dithiolene) complexes, $[Au(qdt)]^-$ (qdt = quinoxaline-2,3-dithiolate) and $[Au(mnt)]^-$ (mnt = 1,1-dicyanoethylene-2,2'-dithiolate), from the correspondent Au(III) salts, $(TPP)[Au(qdt)_2]$ and $(TBA)[Au(mnt)_2]$, in $CH_3CN$ solutions directly injected into the ESI source of the QIT. CID (collision-induced dissociation) of $[Au(qdt)_2]^-$ and $[Au(mnt)_2]^-$ formed by ESI also showed the formation of $[Au(qdt)]^-$ and $[Au(mnt)]^-$, respectively [3]. These Au(I) species reacted promptly with $O_2$ to form $[Au(X)(O_2)]^-$ (X=qdt, mnt) [3] and motivated the present study with nitrogen oxides ($NO_x$). We observed that $[Au(X)(L)]^-$ complexes are formed with L= NO and $NO_2$ but not with $N_2O$. As shown in Fig. 1, $[Au(qdt)]^-$ is clearly more reactive than $[Au(mnt)]^-$ and NO more reactive than $O_2$. For comparison, we tested the reactivity of $[AuCl_2]^-$ with the same neutral molecules (L) but no products were observed.
Theoretical studies of these systems, using DFT methods, were conducted to evaluate the experimental observations. The computed energetics are in agreement with the observed reactivity, indicating that $NO_2$ is the most reactive molecule, followed by NO and $O_2$.
These gas-phase studies may help to better understand the coordination chemistry and reactivity of gold complexes.

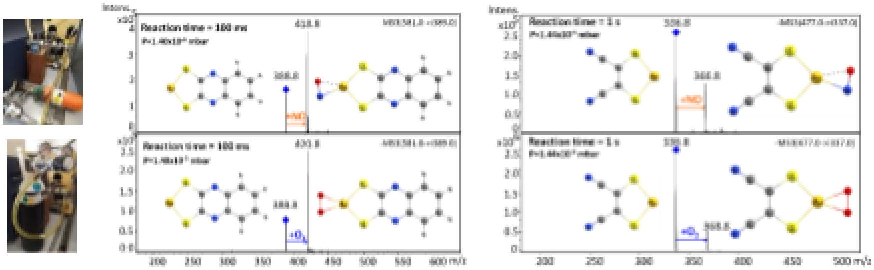

**Figure 1**. Mass spectra showing coordination of NO and $O_2$ to $[Au(qdt)]^-$ (left) and $[Au(mnt)]^-$ (right).

**Acknowledgments:** Centro de Química Estrutural (CQE) 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 (IMS) is an Associate Laboratory funded by FCT through project LA/P/0056/2020. This work was also supported by FCT through projects PTDC/QUI-QFI/31896/2017, UIDB/04349/2020 ($C^2$TN) and UIDB/04046/2020 (BioISI) and through RNEM – Portuguese Mass Spectrometry Network, ref. LISBOA-01-0145-FEDER-022125, also supported by Lisboa2020, under the PT2020 Partnership Agreement, via the European Regional Development Fund (ERDF).

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# P65 Ionic liquids as catalysts for bio-oil production

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This work aims to study the effect of ionic liquids and other conventional solvents on the liquefaction of biomass to produce bio-oil.

The biomass batch liquefaction assessments were carried out in two different approaches, conventional and microwave heating. In the former one, an oil bath or heating mantle provides the heating source, requiring a longer reaction time. On the other hand, when microwave radiation is used as an energy source, the conversion rate is sped up, leading to shorter residence times.

Results and discussion of the performance of different ionic liquids, as well as molecular organic solvents, will be presented, along with the characterisation of the biomass, solvents, and bio-oils.

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# P66 NMR-aided mechanism study of a new Ruthenium complex

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The reaction of 2-di-*tert*-pyridylphosphine (**1**)[1] with [{Ru(COD)$Cl_2$}$_x$],[2] in the presence of triethylamine and hydrogen led to an unexpected complex, **2**, that results from the cleavage of a C-P bond. Concomitantly, a new P-H bond is formed (**Fig. 1**). This complex was fully characterized by solution and solid-state NMR, and single crystal X-ray diffraction. The complex **2** formation mechanism is currently under investigation, through a combination of DFT, NMR and especially designed experiments. We report here our attempts to elucidate the mechanism formation of complex **2**.

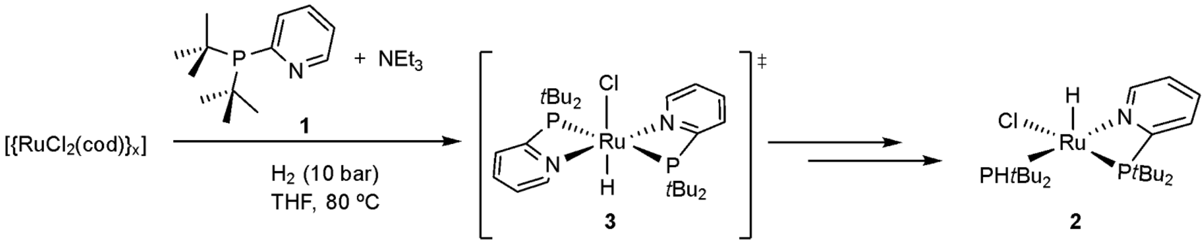

**Figure 1**. Possible pathway for the synthesis of complex **2**.

**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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# P67 Aerobic oxidation of a chalcogen bond donor centre in a copper(II) complex

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Mahmudov, Kamran T.[A,B]; Guedes da Silva, M. Fátima C.[A]
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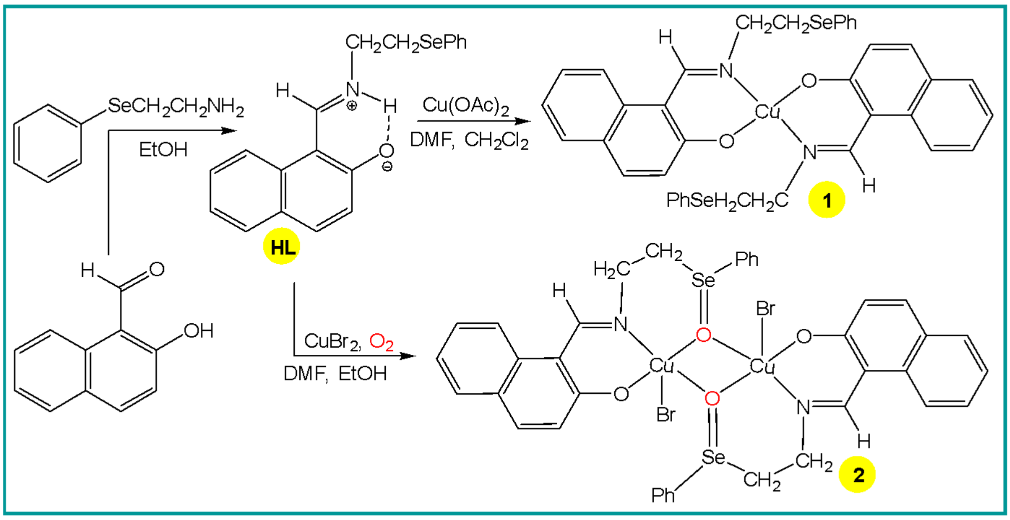
The use of chalcogen bonding (ChB) as an alternative to hydrogen bonding has been reported in many research works associating to a broad spectrum of fields, such as molecular recognition, crystal engineering, catalysis, coordination chemistry, etc. [1−4]. Compared to hydrogen bond and other types of noncovalent interactions, the role of chalcogen bonding has not yet been well highlighted in coordination compounds. Herein, we have synthesized a new ChB donor ligand, (*E*)-1-(((2-(phenylselanyl)ethyl)iminio)methyl)naphthalen-2-olate (**HL**), and its copper(II) complexes **1** and **2** (**Scheme**). In contrast to divalent selenium in **1**, the tetravalent Se atom behaves as a ChB donor between tecton in crystal packing of **2**, leading to 1D network.



**Scheme**. Synthesis of a Schiff base ligand and its 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. KTM and AVG acknowledge the FCT and Instituto Superior Técnico (DL 57/2016 and L 57/2017 Program, Contracts no: IST-ID/85/2018 and IST-ID/110/2018, respectively).

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# P68 Transforming large molecules using surfactant-templated hierarchical ZSM-5 in Friedel-Crafts acylation reactions

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Zeolites are the most important heterogeneous catalysts used in industry. However, the purely microporous nature of these materials hinders their application when large molecules are involved, especially in liquid phase reactions [1]. The surfactant-templated method aims to produce hierarchical zeolites with customized porosity, according to the chosen surfactant and operation conditions [2]. In this work a commercial ZSM-5 zeolite (Si/Al=15) was treated with $NH_4OH$ + CTAB under autogenous pressure at 150 ºC, changing the treatment period between 3 and 48 h. Upon characterization by powder X-ray diffraction and low temperature $N_2$ adsorption isotherms, the samples ZSM5_*t*C, where *t* is the treatment time, were tested in Friedel-Crafts acylation of large substrate molecules with pharmaceutical interest, 1 or 2-methoxynaphtalene with acetic anhydride as acylating agent, using a 1:5 molar ratio, respectively and reaction temperatures of 60 and 80 ºC. Reaction products were analyzed by GC equipped with FID detector. Preliminary catalytic results are presented in **Fig. 1**.

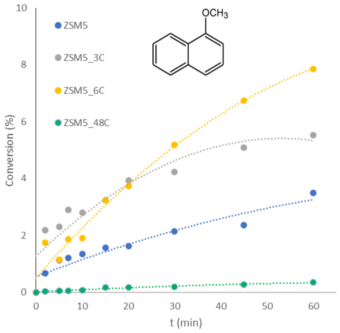

**Figure 1**. 1-methoxynaphtalene conversion as function of reaction time at 60 ºC.

The treatment duration causes structural and textural modifications that impact on the catalytic behavior, 3 and, especially, 6 h are the optimal duration of the surfactant-templated treatment. The effect of other substrates and reaction conditions and currently being studied.

**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. Instituto Politécnico de Lisboa (IPL) through Project IPL/2021/ZeoGemini ISEL.

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# P69 Oxidation of styrene derivatives with iron oxide NP's functionalized with Mo

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In the last few years nanoparticles have been receiving special attention from several research groups. [1,2] Since the advantage of combining nanoparticles properties with magnetism was found, multiple studies have been made concerning heterogeneous catalysis due to its easy separation from the reaction medium only by using an external magnetic field.

Progressing our research on catalytic olefin epoxidation, in the present work magnetic iron oxide nanoparticles were prepared, which were subsequently coated with a silica shell and finally grafted with a pyridine derivative ligand. This allowed coordination with a $[MoI_2(CO)_3]$ organometallic precursor complex. Preparation of these materials was further confirmed by powder XRD, FTIR spectroscopy and SEM and TEM analysis characterization.

Olefin epoxidation is considered one of the most relevant reactions for the industry due to the importance of epoxides in the production of various products such as resins, paints, and surfactants, and are also important intermediates in the production of pharmaceutical products, such as derivatives of styrene oxide. Olefin epoxidation reactions of styrene and related substrates – *trans*-β-methylstyrene and 4-chlorostyrene, were promoted by this organometallic nanomaterial using *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide ($H_2O_2$) as oxidants, dichloromethane ($CH_2Cl_2$), acetonitrile ($CH_3CN$) and toluene (Tol) as solvents and at two different temperatures, 55 and 80 ºC. The catalytic studies showed better results of substrate conversion and yield for the desired product using TBHP as oxidant

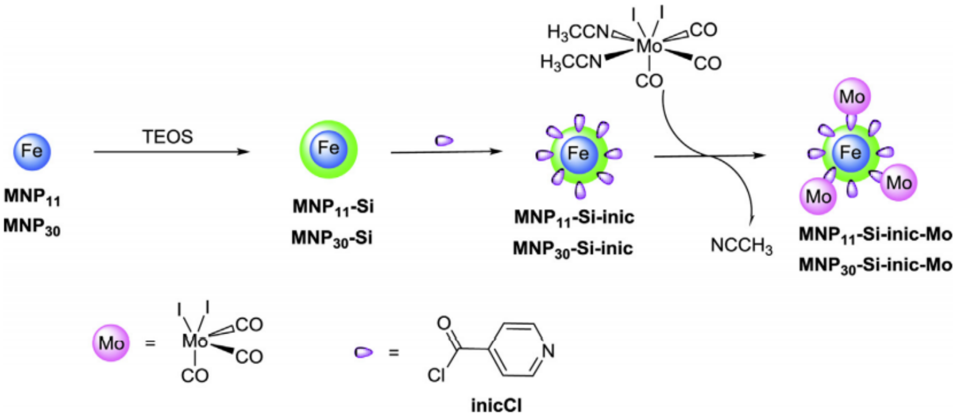

**Figure 1**. Magnetic iron oxide nanoparticles derivatized with a Mo(II) precursor.

**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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# P70 Electroreduction as a solution for $CO_2$ to low-carbon fuels conversion

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As the main greenhouse gas (GHG), carbon dioxide ($CO_2$) is responsible for the increase in global temperature. Regulations on $CO_2$ release are still not enough to reduce the impact of mankind in earth warming. It is necessary a perspective for which the concentration of these gases could be reduced by their capture and reutilization. Electrochemical reduction of carbon dioxide with renewable electric energy sources, or by direct electrocatalytic reduction, could provide a solution in this sense, with additional interest as source of high-value chemical raw materials and chemicals in the future *via* the conversion of $CO_2$.

$CO_2$ electroreduction reaction (CO2ERR) is a challenging route thar aims to contribute to the climate change problematic by an environmental-friendly reduction of $CO_2$ to low-carbon fuels (Methane, ethanol, etc.) by electrochemical methods. To optimize this process, is necessary to employ improved electrocatalyst to overcome the inner problems of selectivity and low efficiency [1]. These catalysts must present high active area, as the reaction is carried out at their surfaces, and conductivity to avoid energy loses by resistance problems. These characteristics are well accomplished by the 3D-metal foams prepared in our group by Dynamic Hydrogen Bubbling Template Electrodeposition (DHBT-ED), a simple, inexpensive, scalable, flexible, and environmentally friendly route. Additionally, the tunability of this method enlarge the possibilities to reach improved selectivity for the conversion.

In this work, metal foams based on Cu are prepared by DHBT-ED and tested as electrocatalysts for CO2ERR. The relation synthesis conditions-conversion performance is evaluated, including the selectivity by means of the faradaic efficiency.

**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 national funding from FCT in the frame of the project PTDC/QUI-ELT/28299/2017. P. Arévalo-Cid also would like to thank FCT for the founding through the contract CEECIND/01965/2018. A. P. C. Ribeiro thanks Instituto Superior Técnico for the Scientific Employment contract IST-ID/119/2018.

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# P71 $CO_2$ conversion with Fe(II) Hofmann clathrates

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The atmospheric carbon dioxide ($CO_2$) concentration has greatly increased in the last decades leading to irreversible climate changes in our planet. Conversion of this gas is an exciting way to tackle this problem, generating different types of products that can be used as fuels or feedstocks (e.g. CO, $CH_4$, CHOOH). $CO_2$ photoreduction became in recent years one of the methods used for this purpose recurring to different catalysts using a wide range of metal complexes. [1,2]

Hofmann clathrates are bimetallic three-dimensional (3D) and two-dimensional (2D) coordination frameworks constituted by Fe(II) ions that are coordinated to cyanometallic anions $[M(CN)_x]^{y-}$ (where M = Ni, Pd, Pt, Cu, Ag, Au, Nb) and N-donor heterocyclic ligands. These supramolecular structures can present different types of properties and be effective catalysts for the $CO_2$ photoreduction. In this work, we synthesized a variety of Hofmann structures using different pyridine derivative ligands (**Figure 1**) aiming at using these structures as catalysts in the $CO_2$ photoreduction. The new structures are characterized by FTIR and UV-vis spectroscopies.

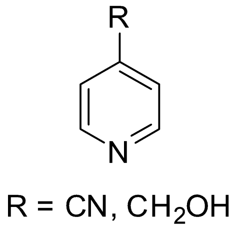

**Figure 1**. Ligands used in the synthesis of Hofmann clathrates.

**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. We are grateful to Fundação da Ciência e a Tecnologia, FCT, for Project PTDC/QUI-QIN/0252/2021. P.N.M. acknowledges FTC for financial support (CEECIND/00509/2017).

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# P72 The NMR facility at CQE

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The NMR facility at CQE is part of the IST-node of the Portuguese NMR Network (PTNMR). It has as main purpose the support of 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 several different probeheads and a 300 MHz dedicated to solid-state NMR.
Over the last 5 years several equipment was acquired to widen the scope of experiments in NMR. These include a 4 mm ss NMR probehead and a broad band Diff60 NMR probehead for the 500 MHz machine, a 7 mm ss NMR probehead (WB) for the 300 MHz ss NMR machine and a high-pressure NMR cell (for pressures up to 1 kbar). A new online booking system was also implemented.

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MEDLife

# P73 New iron-cyclopentadienyl complexes with imidazole ligands: Synthesis and application in cancer therapy

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Cancer is the second leading cause of death worldwide, with estimated 10 million deaths in 2020 [1]. Platinum-based drugs are the most used chemotherapeutics, administered alone or in conjugation with other medications. Yet, one of the major problems of chemotherapy is its low selectivity that leads to severe side effects. Thus, it is of great importance to discover new and more effective treatments [2]. The success of previous works on the development of new iron-based compounds with the general formula $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(\mathbf{L})]^+$, where **L** are different nitriles, against aggressive breast (MDA-MB-231) and colorectal (SW480) cancer cells [3,4] prompted us to change the nature of **L**. In that frame, five new cationic complexes where **L** is 1*H*-imidazole (**1**); 1,3-benzodiazole (**2**); 1-benzymidazole (**3**); 1-butylimidazole (**4**); 1-(2-hydroxyethyl)imidazole (**5**) were synthesized. The choice of imidazole-based ligands was not arbitrary: in addition of being able to easily bind to metallic centers, the imidazole ring is a constituent of several important natural products such as purine, histamine, histidine and nucleic acids, and its structure is present in many drugs with therapeutic activities such as analgesics, antifungals, antivirals and antitumoral [5]. All the complexes were fully characterized by several analytical and spectroscopic techniques. In addition, single crystals of all compounds were successfully obtained. Their anticancer activity was studied in colorectal cancer cells sensitive (Colo205) and resistant (Colo320) to doxorubicin (a drug in clinical use), revealing $IC_{50}$ values in the low micromolar range.

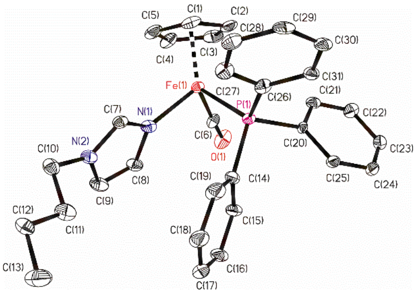

**Figure 1**. ORTEP for the cations complex **4**. All the non-hydrogen atoms are presented by their 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

**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. This work has been financed by the FCT within the scope of project PTDC/QUIQIN/28662/2017. Adhan Pilon thanks FCT for his Ph.D. Grant (SFRH/BD/139412/2018. Andreia Valente acknowledges CEEC-IND/01974/2017 (acknowledging FCT, as well as POPH and FSE - European Social Fund).

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# P74 TBCCD1, a key protein for microtubule anchoring to the centrosome and the kinetochore

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Cellular division is a highly regulated process, whose deregulation has been frequently associated with pathological conditions like tumorigenesis [1,2]. The accuracy of this process requires the involvement of the centrosome and the kinetochore, that are essential for microtubule (MT) anchoring. The centrosome is a MT and actin organizing center in animal cells, important to define the division plane, to assemble/position the mitotic spindle, and as a regulator of the cell cycle [2,3]. The kinetochore is a protein complex responsible for anchoring mitotic/meiotic spindle MTs to chromosomes [4].

Published work from our group identified the centrosomal TBCC domain-containing human protein 1 (TBCCD1) [5]. Later, we found that the gene encoding TBCCD1 originates two splicing variants designated by TBCCD1v1 and TBCCD1v2, which differ in their N-terminal region, but share the functional domains. TBCCD1v1 has a vast proximity interactome enriched in other centrosome/cilia-related proteins required for centrosomal MT anchoring.

Here, we explore the differential functions of the two variants. Using immunofluorescence assays in several human cell lines we observed that TBCCD1v2-GFP localizes only in the cytoplasm. By western blot, we further observed that TBCCD1v2 was only present in the cytosolic fraction, while TBCCD1v1 was present in the cytosolic and nuclear fractions (the latter containing the centrosome). We also determined TBCCD1v2 proximity interactome using BioID [6]. This interactome is composed of 19 proteins that functionally group in kinetochore, MT/cilia, and DNA-binding proteins. Therefore, we further analyzed by western blot assays the impact of TBCCD1v2 levels in its partners localized in the kinetochore. For this we analyzed the levels of CENP-M, a kinetochore protein, in response to TBCCD1v2 overexpression in HEK 293T cells. We observed that TBCCD1v2 overexpression decreases CENP-M levels. It is known that CENP-M is upregulated in tumors [7] and we observed that CENP-M levels are higher in the tumor cell lines HEK 293T and HeLa, than in the non-tumor RPE-1 cells. In HFF-1 primary cells, that divide at a slower rate than RPE-1 cells, CENP-M is present at vestigial levels. Together, these results further support that TBCCD1v2 has a critical role in cellular division, as its levels influence a kinetochore protein. Considering that TBCCD1v1 is important for the MT anchoring to the centrosome and that the kinetochore also anchors MTs, we further hypothesize and aim to study if TBCCD1v2 has a similar role in the MT-kinetochore attachments.

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# P75 Finding new potential inhibitors of PBP2a from methicillin resistant *Staphylococcus aureus*

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Methicillin-resistant *Staphylococcus aureus* (MRSA) is a critical worldwide concern that requires new treatment and management approaches. MRSA is a major cause of nosocomial infections, with a high mortality rate due to multi-resistance to β-lactams. MRSA resistance is related to the acquisition of a PBP2a-coding *mecA* gene; the mecA protein has low affinity to β-lactams, meaning that cell wall peptidoglycan formation is not blocked, and bacteria survive. S. aureus PBP2a adopts a closed active site conformation, inaccessible for β-lactams. This reduced susceptibility to β-lactams is related to both PBP2a changes at a serine nucleophile in the active site and to the presence of a loop protecting the active site from inhibitors. The conformational change of this loop is regulated by an allosteric site distal from the active site, which becomes accessible only when the allosteric site is occupied. Thus, there is a pressing need for innovative antibiotics to control resistance in these strains.

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

Known inhibitor, L-695256, with best results to the target protein presented affinities of -6.2 kcal.mol$^{-1}$ for the allosteric site in the native PBP2a and -9.4 kcal.mol$^{-1}$ for active site of acylated PBP2a protein (PDB:3zg0). Promising hit compounds tested in this work presented significant improvements in affinity for both catalytic sites, for instance, -8.1 kcal.mol$^{-1}$ for the allosteric site in the native PBP2a (PDB:1vqq) and -12.1 kcal.mol$^{-1}$ for active site of acylated PBP2a protein (PDB:3zg0). Hit compounds maintained the expected interactions to the protein has known inhibitors. These obtained lower binding energies for these interesting scaffolds present significant improvements in affinity for both sites. Moreover, binding of one of the most promising hit compounds to the allosteric site induce protein conformational change and subsequently to a more accessible catalytic residue.

These results indicate that tested compounds are promising hits targeting PBP2a protein from MRSA, contributing towards their potential use to overcome β-lactam resistance. Currently, more molecular dynamics simulations are being deployed to understand whether the binding of other hit compounds to the allosteric site can induce protein conformational change, contributing to a more accessible active site.

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# P76 An MS multi-omics approach to drug repurposing – unravelling hidden mechanisms of drug action

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Drug development can proceed by *de novo* drug design, rational drug modification, or, as it happens more often recently, by drug repurposing. In the latter approach, any given drug can be tested for use towards a target different from the original one. Off-site drug action and adverse drug reactions can be good indicators of drugs worthy of repurposing.

Montelukast (MTK, Singulair) is routinely used for asthma management. MTK displays sporadic peripheric side-effects, which promptly resolve upon stopping the treatment, but is also associated with mild-to-severe neuropsychiatric effects, particularly in children. Interestingly, MTK is being considered as an alternative therapy towards Alzheimer's Disease.

In order to reconcile the central nervous system (CNS) adverse reactions to MTK with its repurposing for a neurodegenerative condition, we performed a multi-omics multi-system MS-based evaluation of the pathways involved in the response to MTK administration using an *in vitro* embryonic chicken neuron model and an *in vivo* approach using a rodent model. Taking advantage of the high-resolution mass spectrometry equipment installed at CQE Mass Spectrometry Lab, full untargeted metabolomics and proteomics approaches were used to study both models' response to MTK.

Results clearly show that MTK treatment is associated with an hyperactivation of the HPA axis, leading to a dysregulation of neurotransmitter-dependent pathways, establishing a clear relation between MTK and the described adverse reactions on the CNS. Furthermore, proteomics data also suggest that MTK influences endopeptidase activity, apoptotic processes, and cell death.

In parallel, thiol-based oxidative stress-protection pathways were found shifted towards an increased global oxidative status. This result correlates with the identification of an MTK-glutathione adduct formed by both enzymatic and non-enzymatic pathways, also completely characterized by HRMS in this work.

To conclude, the network connectivity between both omics approaches supports the relation between metabolites and proteins in pathways influenced by montelukast.

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# P77 Evaluation of the therapeutic potential of isoniazid derivatives against tuberculosis: membrane interaction studies

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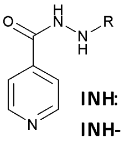
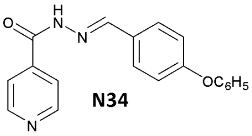
Tuberculosis is an infectious disease caused by *Mycobacterium tuberculosis* (*Mtb*) which, despite being preventable, and mostly curable, is still one of the leading causes of mortality worldwide. This is due to the growth of multi-drug resistant strains unsusceptible to currently available therapies. Since INH is still one of the most powerful anti-tubercular drugs, a series of isoniazid derivatives were synthesized [1, 2], having shown, in recent studies, to be valid leads to overcome drug resistance in tuberculosis [2].

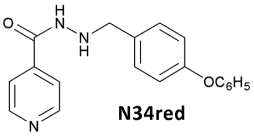
In this work, we selected four compounds, INH, INH-$C_{10}$, N34 and N34red to study their interaction with different membrane model systems by steady-state and time-resolved fluorescence spectroscopy and the use of fluorescent membrane probes.



**INH**: R= H
**INH-$C_{10}$**: R= $CO(CH_2)_8CH_3$



**N34**



**N34red**

Three biomembrane models were evaluated: two single-component systems, a gel and a fluid lipid bilayer, studied with the probes *t*-Pna and di-8-ANEPPS, and a ternary lipid bilayer containing sphingomyelin and cholesterol to mimic the mammalian plasma membrane, namely the presence of lipid rafts, studied by Förster's resonance energy transfer (FRET). In the one-component models, studies with *t*-Pna revealed that all INH derivatives, especially INH-$C_{10}$, caused a disturbance in the packing of the acyl chains in the lipid gel phase, with no effect on fluid membranes.The probe di-8-ANEPPS disclosed that all INH derivatives, and INH itself, caused a disturbance of the membrane dipole potential, in both fluid and gel bilayers, suggesting an insertion at a superficial level of the biomembrane, the most pronounced effect being observed for N34. Additionally, using FRET, it was possible to determine that none of the compounds influenced the size and organization of the membrane lipid domains.

These results indicate that all compounds can incorporate into both gel and fluid lipid membranes, and that INH-$C_{10}$, in particular, incorporates deeper into gel membranes. This suggests that INH-$C_{10}$ might be able to incorporate into other dense membranes, such as the mycolic acids-rich *Mtb* cell wall, which could facilitate its delivery to the therapeutic target. FRET results indicate that both INH and INH derivatives can incorporate in human cell plasma membrane without disturbing its lipid domains organization which is a good indicator of their therapeutic potential.

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# P78 Conventional vs. microwave- or mechanically-assisted synthesis of dihomooxacalix[4]arene phthalimides

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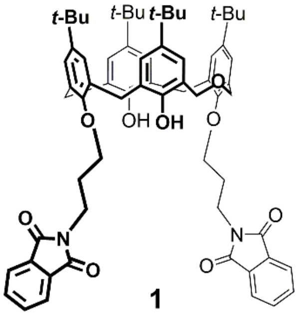
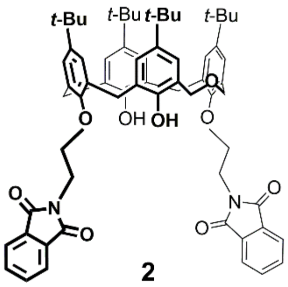
Since the late 1980's, the microwave (MW) technology has become a very important tool in a wide range of chemical reactions [1]. This technique provides uniform heating of the reagents throughout the reaction vessel, allowing a rapid and homogeneous heat transfer. MW heating drastically reduces reaction times compared to conventional heating. Higher product yields, higher reaction selectivity and low waste are other advantages of this technique, as well as the use of less or even no solvent and catalyst. Ball milling (BM), another environmentally friendly methodology applied to organic synthesis under solvent-free conditions, has also been developed mainly in the last decade [2]. Calixarene-based molecules are amongst the most investigated frameworks in host-guest and supramolecular chemistry [3]. Both techniques have been employed in the synthesis of calixarene hosts.

In the course of our research on anion binding by ureido-dihomooxacalix[4]arenes [4, 5], we were interested in studying the introduction of urea binding sites into the 1,3-positions of the calixarene lower rim through propyl or ethyl spacers. It is known that *O*-alkylation reactions of calixarenes by conventional methods can take long times and produce low yield products. Thus, MW irradiation and BM were employed in this work to obtain the target 1,3-disubstituted phthalimides (**1** and **2**), which have been prepared as precursors to urea-terminated anion-binding macrocycles. Other differently substituted derivatives were also obtained, and the determination of some photophysical properties are also presented.



**1**



**2**

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# P79 Evaluation of the toxicity of synthetic cathinones used as drugs of abuse

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In the last decade, an increased consumption of new psychoactive substances (NPS) as drugs of abuse has been globally verified. Because these substances are new psychoactive compounds they are not part of the list of controlled substances. Furthermore, the emergence of a wide range of NPSs was driven by the introduction of small changes in the basic structure of the initial drug, thus allowing these derivatives to circumvent legal restrictions.

NPSs represent a threat to public health since they intend to mimic the effect of an illicit drug, however other effects associated with their consumption are still unknown and 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 present in the *Catha edulis* plant. [2] Evidence indicates that the consumption of synthetic cathinones may be associated with several adverse neurological effects including agitation, dizziness, depression, hallucinations, and even death, due to intoxication and/or liver damage, however, there is still a lack of knowledge about the biological and toxicological aspects of these NSPs.

This work aimed to increase knowledge about synthetic cathinones, hence new cathinones were synthesized having been structurally characterized by NMR and HRMS. The potential biological effect of 20 cathinones were assessed *in vitro* using liver cancer cell line HepG-2 and on enzyme acetylcholinesterase (AChE), often associated to neurotransmission.

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# P80 New ruthenium-based complexes for specific therapy of colorectal cancers with KRAS mutation

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Colorectal cancer (CRC) is the second leading cause of cancer death and the third most common malignancy in the world [1]. One particular type of CRC is the one that harbors KRAS mutations, which account for almost 40% of CRCs. CRC harboring KRAS and overexpressing EGFR are resistant to EGFR inhibitors therapy, which constitutes a clinically relevant problem that needs new therapeutic approaches [2]. Moreover, KRAS hotspot mutations specific targeting is very difficult to achieve, highlighting the need of developing new specific target drugs. To overcome these limitations, the Bioinorganic Chemistry and Drug Development (BIOIN) Group from FCUL has developed a family of ruthenium organometallic-based complexes with promising therapeutic potential for KRAS-mutated CRC. This family of complexes was designed using macromolecules and/or biomolecules to increase the targeting for CRC cells. In this work, we aimed to evaluate the anticancer effects and mechanism of action of these new Ru complexes in CRC-derived cell lines harboring KRAS mutations by studying *in vitro* cell viability, proliferation, cell death mechanism, migration, intracellular distribution, actin cytoskeleton alterations, and KRAS signaling pathway molecules expression (the most important signaling pathway for CRC carcinogenesis). The “lead compound” was selected to explore the preclinical *in vivo* “proof of concept” for CRC therapy.

Our results revealed that all Ru agents are selective to CRC cells, decrease proliferation, induce apoptosis, decrease migration, and have different distributions in CRC cells. The “lead compound” also affected the actin cytoskeleton and inhibited KRAS and KRAS downstream signaling molecules expression. In the *in vivo* studies, a toxicity study was performed to determine the maximum tolerated dose of the “lead compound” to proceed with histological analysis of various organs, biochemical analysis of the blood, and tumorigenesis assays.

Overall, the new Ru-cyclopentadienyl agents are promising drugs for CRC therapy, which could bring new exciting therapeutic avenues for specifically target CRC harboring KRAS mutations.

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# P81 Small-scale peptide production with recombinant DNA technology

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Peptide synthesis is traditionally an automated process, that affords mg quantities of peptides up to 20 or 30 aminoacyl residues. However, it is a costly process, and larger sequencies are increasingly harder to obtain.

To tackle this problem, we have employed two different PCR-dependent DNA cloning strategies. In the first case we tried to produce a 42-amino acid peptide, corresponding to the *N*-terminal sequence of the β-amyloid protein. For this, two primers, corresponding to the full cDNA sequence of the gene region encoding this peptide, were PCR-amplified and inserted through exonuclease-digestion into a pET28a(+) vector. Upon transformation into E. coli cells, the peptide was successfully expressed and purified by immobilized metal affinity chromatography.

In the other approach, a radically different cloning strategy was employed to obtain peptides starting at 6 aminoacyl residues. In this strategy, two 40 bp-long primers, identical to the cloning site of the pET28a(+) expression vector, were designed, featuring small 3'-overhangs containing the cDNA encoding the peptide of interest. These two primers were PCR-amplified with a high-fidelity DNA polymerase, and the product was then used as starter oligos for an overlap extension PCR approach, using the expression vector as template, and affording the expression vector with the desired insert as product. All remains of the original (without insert) template were removed by DpnI digestion, and the final products were transformed into expression-ready *E. coli* cells. This workflow required no transformant selection, and afforded expression clones of each peptide.

These two approaches show that recombinant DNA technology can be easily used for small scale peptide production at a large range of peptide lengths, with fewer costs, opening the doors to the production of peptides for structural studies, medicinal chemistry targeting and other applications that require small portions of these molecules, but high confidence on their sequence.

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# P82 Electrochemistry and evaluation of cytotoxic and AChE inhibition activities of 1,4- and 1,2-naphthoquinone derivatives

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Naphthoquinone (NQ) derivatives have been highlighted in the field of new compounds for pharmaceutical applications. This rising interest lays on their diverse biological and medical properties, such as anti-tumoral and anti-inflammatory activities [1,2]. Their mechanisms of action are often related to its redox properties, as most have the capacity to accept one or two electrons generating highly reactive radical species capable of interacting with biological molecules such as DNA, enzymes, and other proteins [3]. In this work, the electrochemical properties of various 1,4-NQ and 1,2-NQ derivatives (Figure 1) were studied and correlated to their biological activities, namely cytotoxicity against human liver cell lines (HepG2) and acetylcholinesterase (AChE) enzyme inhibition activity. Also *in vitro* results were compared and correlated with *in silico* studies to better understand the biological properties of the NQ derivatives, particularly enzyme-inhibitor molecular interactions. It was observed that both 1,4-NQ and 1,2-NQ substituted naphthoquinones exhibited improved biological properties than their base structures. In general, 1,2-NQ derivatives showed a higher cytotoxicity activity and inhibition capacity against AChE than similar 1,4-NQ derivatives. Biological activities were seen to be correlated with electrochemical data. Molecular docking scores were determined using AutoDock Vina v.1.2.0, revealing higher scores for the compounds that showed higher inhibition against AChE, resulting from interactions with CAS and PAS binding sites on AChE catalytic cavity causing blockage of the active site gorge.

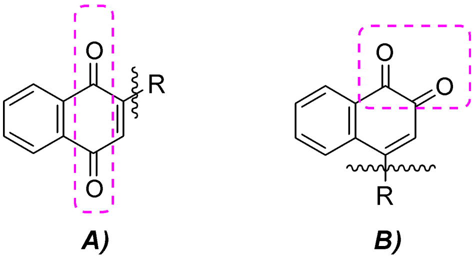

**Figure 1**. Structural feature of ***A)*** 1,4-NQ and ***B)*** 1,2-NQ derivatives.

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# P83 Ribonucleosides stability and prebiotic synthesis

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The *RNA World hypothesis* is the model that best describes the origin of life. [1] Nevertheless, it has not yet been possible to establish a consistent and unified chemical synthesis pathway of RNA. [1] With the detection of organic molecules in meteorites with high carbon content, some proposals focus on extraterrestrial bodies as potential carriers of molecules for the emergence of life on Earth. [2] Despite the wide variety of organic molecules in meteorite samples, ribonucleosides, essential for the aforesaid hypothesis, were never detected, as opposed to corresponding nucleobases. [2] Studies indicate that the entry of a meteorite into the atmosphere induces the formation of chemical reactions, especially the degradation of organic compounds. [3] Moreover, our research group proved that ribose degradation could occur by the action of carbonate ions, which is one of the meteorite oxidation compounds, induced by current atmosphere. [4]

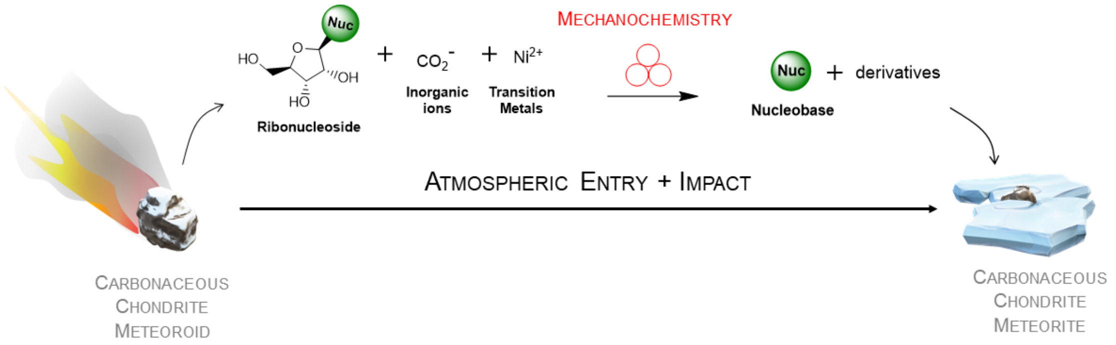

**Figure 1**. Degradation model of ribonucleosides in their respective nucleobases and analogs by the action of mechanochemistry, intensified by inorganic ions and transition metals.

Therefore, the degradation of ribonucleosides to nucleobases could be simulated by mechanochemistry, in presence of carbonate ions and transition metals, explaining in this way, the lack of ribonucleosides in meteorite samples. In addition, the degradation mechanism promoted by carbonate ions can be addressed with computational models, by DFT/TDDFT methodologies, modeling the structures of ribonucleosides, their degradation products, and reactive intermediates. By optimizing this model and comparing it with a real asteroid sample without mechanochemical activity with Earth atmosphere (Bennu, from OSIRIS-Rex mission or Ryugo, from Hayabusa2 mission), it could be possible to detect ribonucleosides, thus proving that the direct synthesis of ribonucleosides by reaction of ribose and nucleobases is not a favorable step for the prebiological evolution of life.

**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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# P84 DNA binding constant determination: what about the uncertainty?

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The determination of thermodynamic constants for the binding equilibrium of substrates to DNA is a common procedure when characterizing the biological activity of metal complexes. Such information is relevant when determining their potential application as anti-cancer drugs. Comparing DNA binding constants from different drug candidates can help explain their effectiveness, but such comparison cannot be done without an estimation of the associated uncertainty.

The network COST Action CA18202 – Network for Equilibria and Chemical Thermodynamics Advanced Research - is dedicated to compiling the best practices in the determination of equilibrium constants. In this framework, an interlaboratory study was organized with the objective of identifying good practices in the determination of binding constants with DNA and designing a “golden standard” procedure for a model system. The chosen system was ethidium bromide (EB) – calf thymus DNA (ctDNA). In spite of the well-known toxicity of EB this system was elected over cianine dyes, porphyrins, schiff bases and ruthenium complexes due to the availability and affordability of both EB and ctDNA, the possibility of fluorescence measurements avoiding UV light detection, which may be harmful to DNA, the absence of serious substrate aggregation and the relatively simple and known intercalation binding mechanism.

The interlaboratory study opens the possibility of identifying, isolating and quantifying the different sources of variability affecting the binding constant determination. This has been done following an approach based on the ISO recommendations, the GUM - Guide to the Expression of Uncertainty in Measurement [1].

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# P85 Synthesis of potentially bioactive azido/guanidino nucleosides

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Synthetic nucleosides, nucleotides and their analogs/mimetics have attracted much attention in organic and in medicinal chemistry, due to their propensity to exhibit a variety of biological properties. Various examples of nucleoside and nucleotide analogs achieved clinical application as anticancer or antiviral drugs, acting through interference with nucleic acid biosynthesis [1]. The ability of these types of molecules to show antimicrobial effects [2] or to inhibit cholinesterases [3] has also been reported. The search for new structures of nucleos(t)ide analogs that may potentiate innovative mechanisms of action and open new therapeutic opportunities remains of interest.

In this context, in this communication we report on the synthesis of novel 5-azido/guanidino nucleosides based on a xylofuranose template. The synthetic pathway employed diacetone-D-glucose as precursor and involved the access to an acetylated 5-azidoglycosyl donor and its further N-glycosydation with uracil or with a purine derivative. Conversion of the azido nucleosides into their guanidino derivatives was then exploited. An interesting result during the synthesis of the glycosyl donor precursor was the access to an imino sugar via an intramolecular Boyer reaction. Herein our results will be presented and discussed.

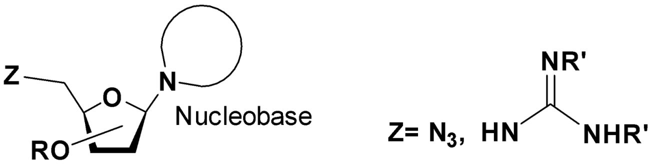

**Figure 1**. General structures of the synthesized nucleosides.

**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 also supported by FCT through project EXPL/MED-QUI/1017/2021 and grant CEECIND/03881/2018.

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# P86 Study of the anticancer activity of silver camphorimine complexes focused on HOS cell line

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The ongoing studies on the biological properties of camphor derived complexes show that they can act as anticancer and/or antimicrobial (bacteria or fungi) agents according to the characteristics of the metal core and the camphor derivatives used as ligands [1-2].

The design of complexes that encompass both anticancer and antimicrobial properties with acceptable toxicity is one of the targets of this project that aims at utilizing camphorimine complexes to functionalize biocompatible materials (ceramic or polymeric) to be used in bone reconstruction or as implants.

In our days, treatment of bone diseases due to trauma, infections, cancer, or other pathologic conditions mostly rely on surgery and chemotherapy which are sometimes compromised by infections. Thus, functionalization of materials (hydroxyapatite or others) commonly used in bone reconstruction with additional anticancer and / or antimicrobial properties is of utmost relevance, since such type of diseases highly compromise the quality of life of elderly population whose number increases with longevity increasing.

So far, a set of silver camphorimine complexes $[Ag(NO_3)L]$ and $[Ag(NO_3)L_2]$ whose antimicrobial properties were assessed before [3] were probed for cytotoxic activity towards HOS cell line showing that complexes with bicamphor type ligands ($L^B$) display high anticancer activity according to the measured Inhibitory Concentration ($IC_{50}$; *ca*. 3.0 μM) for 24 h exposure.

Functionalization of hydroxyapatite with the most active complexes, characterization of the chemical and morphologic properties of the new materials (composites) and evaluation whether the complexes remain biologically active are in progress.

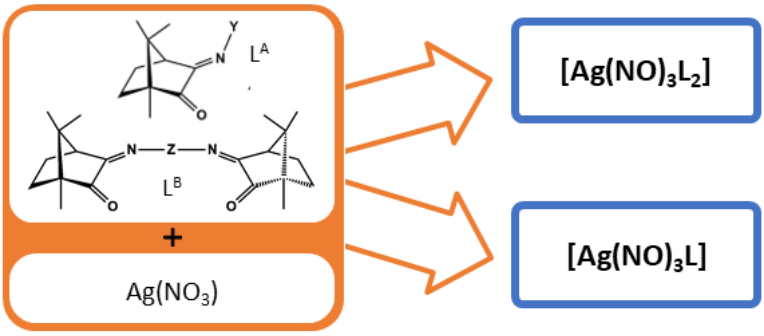

**Figure 1**. Scheme of the ligands and metal used to synthesize the mentioned complexes.

**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. Financial support by FCT through the PhD Grant to Joana Costa (UI/BD/152244/2021).

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# P87 1 plasmid, 4 enzymes – Simultaneous ligase-independent cloning of cytochromes P450 and NADPH oxidoreductase

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In man, drug metabolism is carried out by several enzymes, of which cytochromes P450 (CYPs) are among the most relevant, due to its ubiquity, large substrate specificity and high catalytic activity. CYPs are oxidoreductases that catalyze various chemical modifications of drugs and other xenobiotics, using NADPH as an electron donor. Electron transfer from the cofactor is mediated by NADPH oxidoreductase.

As an approach to obtain these proteins in high quantities for *in vitro* drug metabolism studies, a recombinant DNA approach was employed. Briefly, the coding regions of CYP isoforms 2C8, 2D6, and 3A4, three of the major drug-metabolizing enzymes, were PCR-amplified with high-GC specific primers. Primers were designed to allow for subsequent ordered ligation of the amplification products.

Upon amplicon isolation and purification, a ligase-independent cloning strategy was used to insert all four inserts simultaneously into a kanamycin-resistant pHTP vector, in fusion with a green fluorescent protein. In parallel, individual gene cloning was also performed.

Upon successful transformation into *E. coli* BL21(DE3) cells, proteins were expressed and purified for further activity studies. These include the profiling of their specific activity towards model drugs, to ascertain their metabolizing potential. The metabolites produced by these isolated proteins will be compared with those reported in the literature, in terms of structure and relative abundance, to determine the successful production of functional human CYPs with future use in high-throughput xenobiotic biotransformation/bioactivation studies.

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# P88 Covalent modification of human serum albumin by corticosteroids

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Although reducing the prevalence of hypertension (HTN) is a top priority of the World Health Organization (WHO), the resistance to treatment (RHTN) constitutes a major morbidity/mortality factor of HTN. The association between HTN and abnormal levels of adrenal gland steroids (AGS) has long been recognized. Additionally, elevated levels of AGS were demonstrated to constitute risk factors for both RHTN and Chronic Kidney Disease (CKD).[1] Therefore, a large percentage of the population would benefit from efficient management of AGS-promoted adverse effects. However, there are no suitable methodologies for HTN differential diagnosis which difficult the application of the right medicine strategy.

The covalent modification of proteins by endogenous metabolites is widely recognized not only as an underlying mechanism at the onset of diseases[2] but also an opportunity for the development of diagnosis tools. The fact that AGS have as common structural moiety an acyloin group, led us to investigate if AGS could modify covalently proteins. Human Serum Albumin was incubated with different corticosteroids to investigate this hypothesis. The use of high resolution mass spectrometry-based adductomics tools enabled the identification of irreversible modifications of lysine residues with multiple corticosteroids, *via* Heyns rearrangement (**Figure 1**). The synthetic standards prepared and the analytical methodologies herein developed are anticipated to have a huge impact in several fields of science, by allowing a better understanding of the molecular mechanisms of AGS-induced HTN and CKD, which is key for the identification of new drug targets and risk factors. Additionally, the methodologies developed can be explored as diagnosis/prognosis tools.

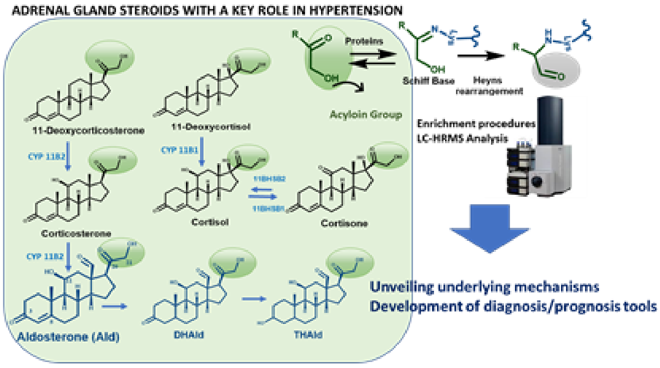

**Figure 1**. Adrenal gland steroids (AGS) containing acyloin functional group play react with lysine residues of proteins via Heyns rearrangement, yielding an irreversible covalent modification.

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# P89 NADPH oxidoreductase sub-cloning and expression

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Over the years, heterologous expression of recombinant proteins has been a very important field in biotechnology, with various laboratory and industrial applications, from protein expression for structural and functional studies to the large-scale industrial production of proteins, such as insulin, that are used as therapeutics. Protein heterologous expression is intrinsically connected to recombinant DNA technology, which allows the manipulation of the genes involved in protein expression, thus virtually enabling the production of any protein in appreciable amounts.

This work aims to establish bacterial strains able to consistently express human proteins involved in drug metabolism for subsequent use in *in vitro* drug biotransformation studies. By resorting to cDNA sub-cloning, the NADPH:cytochrome P450 oxidoreductase (POR), an enzyme essential in phase I metabolism of drugs, xenobiotics and endogenous compounds, was cloned into a Kan-resistant pET28a(+) expression plasmid, with terminal His-tags to allow for Ni-based immobilized metal affinity chromatography, and a TEV-consensus site for selective *N*-terminal His-tag release.

Upon transformation into *E. coli* BL21(DE3) HiControl cells, the POR protein was successfully expressed as a 77 kDa polypeptide present in the membrane fraction. Subsequent work-up of the cell lysates allowed retrieving a purified POR fraction. Protein identity was confirmed by spectroscopic techniques and functional studies are ongoing to fully characterize the cloned protein and its function. In the future, this system will be used to maximize the reliability of an enzymatic reactor for drug metabolism studies, focused on drug toxicity evaluation and prediction.

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# P90 Development of amino(bis)phenolate metal-based compounds for cancer therapy

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Cancer is a disease with a high burden given its wide incidence and high societal impact. Despite the effort invested in its prevention and in research directed to drug development, cancer is still a leading cause of death with almost 10 million deaths in 2020 [1]. With such concerning statistics, the search for effective and safe treatments (surgery, radiotherapy, and/or systemic therapy) [1] is of uttermost importance. Chemotherapy stands out as the most often used therapy much due to the high efficacy of platinum-based drugs, which are employed as the first line treatment in over 50% of cancer cases [2].

Research on new agents with improved efficiency and better tolerance set to overcome the limitations of cisplatin and its analogues (such as severe side-effects and resistance to treatment) [2] is now an intense field of investigation. In this quest, compounds bearing metal ions such as iron, ruthenium and vanadium have been proposed as possible drug candidates. While ruthenium complexes have clearly stood out in this field [3,4], showing a lower systemic toxicity and high activity even against cisplatin resistant tumors, iron and vanadium complexes have been shown to be very promising as well. The set of ligands binding the metal ion is vital to define the biological effect of the overall compound, a feature now well understood for some Ru(II) and Ru(III) families of complexes with different modes of action, depending on the structure and ligands involved [5,6].

The amino(bis)phenolate structure, robust and suitable for metal ion chelation, has emerged as a set of great therapeutic potential. Of the several compounds reported, complexes of V(V) [7], Fe(III) [8] and Ru(II/III) [3,4] with amino/(bis)amino(bis)phenolate ligands are still scarce and roughly unexplored. Ru(III) complexes bearing salicylidene derivatives and (1*R*,2*R*)-cyclohexanediamine were reported to have very promising features as anti-tumor drug candidates [3], and the position of the substituent in the phenyl ring seemed to play a key role in their biological response [5,6].

In this work, we focus on the synthesis of metal complexes bearing the (bis)amino(bis)phenolate structure (that is active on its own with its cytotoxicity being enhanced upon chelation) and metal ions V(IV), Fe(III), and especially Ru(III) (to expand the set of Ru(III) compounds already reported) with the goal to evaluate both the impact of different metal ions and of small changes in the ligand structure on the cytotoxic activity/selectivity, and overall biological response of the complex.

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# P91 Analytical performance of a piezoelectric biosensor for uric acid determination based on different surface modifications

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The present work deals with the development of a piezoelectric biosensor for uric acid determination in urine [1]. The biological recognition element consisted of polyclonal antibodies against uric acid, which was immobilized on the surface of a piezoelectric quartz crystal (native resonance frequency of 10 MHz) with 14 mm in diameter, covered with gold electrodes on both surfaces. The immobilization procedure of the biorecetor included the initial preparation of a self-assembled monolayer of acid 11-mercaptoundecanoic acid on the sensor surface, activated with a mixture of N-Hydroxysuccinimide and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide. The experimental conditions inherent to the formation of the biolayer were optimized based on an analysis of variance (ANOVA) according to a $2^3$ factorial planning. The biosensor´s analytical performance was characterized and compared following the piezoelectric surface modification in the presence and in the absence of protein A [2]. The presence of this protein in the recognition biolayer, allowed a more favourable antibody orientation and thus a significant optimization of several figures of merit such as, limit of detection, limit of quantification, linear response range, sensitivity and response time.

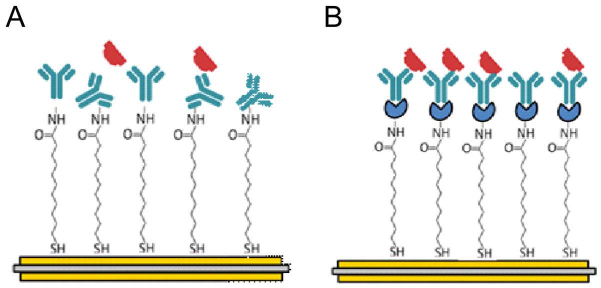

**Figure 1**. Effect of protein A on antibody orientation towards the specific antigen.

**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. Instituto Politécnico de Lisboa: financiamento no âmbito da 5ª Edição dos projetos (IDI&CA) 2020.

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# P92 Cloning and expression of the natural cytotoxicity receptors – a tool for novel immunotherapy drugs

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Natural killer cells are a sub-set of peripheral blood mononuclear cells involved in the innate arm of the immune system. They constitutively express various cell surface receptors that are triggered by the binding of specific ligands e.g. tumour cell-derived proteins, for example, and activate the secretion of cytotoxic mediators including TNF-α, IFN-γ, perforins and granzymes. These constitute a target cell-directed response that is critical in the process of immunosurveillance.

Within the global goal of developing new drugs able to activate the innate immune system, focusing on obtaining small ligands, easily affordable, and with low predictable toxic side effects, we have been cloning the whole set of natural cytotoxicity receptors (NCRs), as well as their ligands.

A traditional cloning approach has been employed in order to obtain stable E. coli strains expressing NCRs. NCR2 (NKp44), NCR3 (NKp30) and NCR4 (NKp80) have been successfully cloned into the pET expression system. These recombinant proteins will be used to develop ELISA assays to probe the affinity of new and known ligands for each receptor. This strategy encompasses the passive immobilization of the purified proteins in polycarbonate plates followed by incubation of said functionalized surfaces with known specific and unspecific ligands, followed by total protein quantification to identify positive binders for each receptor and validate the assay. Selected prototypical ligands of these receptors have been cloned and expressed, namely NCR3LG1 (B7-H6), the natural NCR3 ligand, and AICL, one of the endogenous NCR4 ligands.

Once validated, the functionalized plates will be used in high-throughput ligand scouting assays for each receptor, resorting either to spectroscopic assays to quantify the bound ligands, or to mass spectrometry techniques to identify new ligands.

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# P93 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 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 partially funded through FCT grants SAICTPAC/0019/2015 and PTDC/QUI-QAN/32242/2017.

# P94 Evaluation of Jijel city's (Algeria) honey in terms of quality and authenticity based on the melissopalynology and physicochemical analysis and their antioxidant powers

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Honey is a sweet and flavorful animal product that comes from nectar and/or honeydew. It is used in different nutritional and therapeutic fields. This study aimed at the determination of the botanical origin, the physicochemical characteristics, and the antioxidant activities of two honey samples from two locations in Jijel City (Algeria). The analyzed honey complies with the standards of the Codex Alimentarius Commission. Pollen analysis showed that honey sample H1 was polyfloral and honey sample H2 was monofloral. Quality parameter analysis revealed that moisture content varied from 13.21 to 16.44%. The average pH was 4.34, and the electrical conductivity was 0.56 mS/cm. Protein, proline, and HMF contents were 32.08 mg EBSA/ 100 g, 435.47 mg/kg, and 3.49 mg/kg, respectively. Both analyzed kinds of honey were levorotatory. Phenolic compounds and flavonoids were found to be higher in honey H1 with 60.93 mg of EAG/100g and 20.92 mg of EC/100g, respectively. Results of antioxidant activities showed that honey H1 was much more effective in reducing iron and copper than honey H2 and gave the best total antioxidant capacity. In addition, the study of the antiradical activity against DPPH and ABTS revealed that honey H1 was able to scavenge DPPH and ABTS radicals with 48.88 and 18.21 %, respectively.

**Keywords:** honey, physicochemical properties, pollen analysis, phytochemical analysis, antioxidant activity.

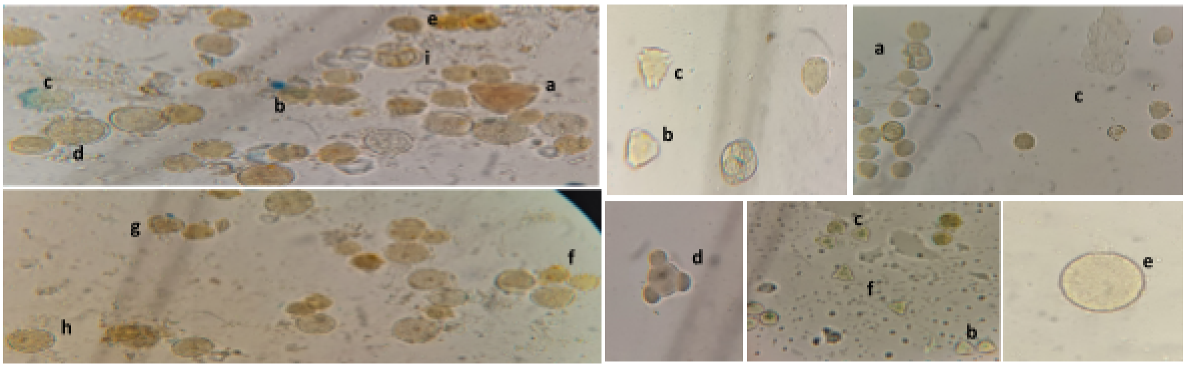

**Figure 1.** Pollen grains of honey under optical microscope (G x 40).

**Acknowledgments:** Rabha Aayad acknowledge the Algerian Ministry of High Education and Scientific Research for sponsoring this work and Maria Eduarda Araújo acknowledge FCT financial support through the project LA/P/0056//2022.

# P95 Molecular design of halogenated glycosides as tools to study protein–carbohydrate interactions

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The molecular recognition of carbohydrates by proteins is involved in numerous biological processes of medicinal interest. Therefore, the design of sugar mimetics occupies a key role in chemical biology [1] and drug discovery [2]. Whereas a range of intermolecular interactions have been reported as effective modulators of protein-carbohydrate recognition events, the potential of halogen bonding [3] has been markedly underexploited in this scope, despite the increasing relevance of this type of interaction in medicinal chemistry and other fields [4].

In this work, we investigated the potential of halogen bonds (XBs) to act as mimetics of intermolecular interactions commonly involved in protein-carbohydrate binding (**Figure 1**), aiming at expanding the chemist's toolbox in the search for novel modulators of therapeutically relevant carbohydrate-recognizing proteins. This was accomplished through the computer-aided design and synthesis of glycosides bearing halogen substituents at key positions of the sugar in order to direct their XB-mediated interaction with known biological acceptors. The main results obtained will be disclosed and their implications discussed.

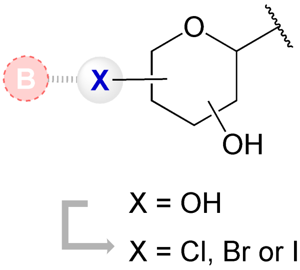

**Figure 1**. Schematic representation of the strategy described in this work. B = Lewis base in a protein system.

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This work was also supported by FCT through doctoral fellowship SFRH/BD/116614/2016 (RN) and grants CEECIND/03881/2018 (NMX) and CEECIND/00381/2021 (PJC).

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# P96 Targeting P-gp with Ru-cyclopentadienyl compounds: an approach to overcome cancer multidrug resistance

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The occurrence of multidrug resistance (MDR) is one of the most challenging obstacles in cancer treatment. For metastatic cancers, approximately 90% of patients are unresponsive to therapy because of MDR [1]. One of the main mechanisms of MDR is the overexpression of ATP Binding Cassette (ABC) efflux transporter proteins that pump drugs out of the cells leading to a reduction in effective intracellular drug concentrations. To overcome this limitation, a current hot topic in chemotherapy research includes the development of inhibitors of these ABC efflux pumps to sensitize cancer cells to drugs [2]. Our group has been engaged in the development of “Ru-cyclopentadienyl” (“RuCp”) drugs with transporter proteins inhibitory properties [2-4]. From our data set, we highlighted two compounds with remarkable cytotoxic activity for breast and ovarian cancer cells and the ability to inhibit P-gp and MRP1 exporters, respectively [3,4]. In a recent structure-activity study, fourteen compounds with general formula $[Ru(\eta^5-C_5H_4R)(bipy)(PPh_3)]^+$ (being R= -H, $-CH_3$, -CHO, $-CH_2OH$ or $-CH_2$Biotin and bipy = 2,2’-bipyridine functionalized ligands) were tested against four types of non-small cell lung cancers (NSCLC) with different expression levels of P-gp and MRP1 transporters namely, A549, NCI-H228, Calu-3 and NCI-H1975. Among them, six compounds presented remarkable activity against cisplatin-resistant NSCLC cells. Investigations on the mechanism of action of these compounds showed that, when administered at non-cytotoxic doses, they were able to increase cisplatin cytotoxicity in resistant cells by targeting P-gp and MRP-1 transporters, thus inducing collateral sensitivity. Molecular docking calculations with a set of RuCp drugs helped to identify the best binding pockets in P-gp and correlate their binding affinities with the experimental data. Using *in silico* and cell-based studies, we show how small modifications in the compounds’ structure drastically affect the anticancer activity against NSCLC.

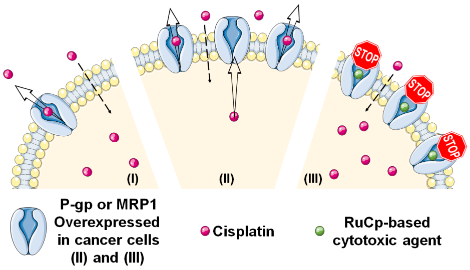

**Figure 1**. “RuCp” compounds increase cisplatin activity by inhibiting efflux pumps.

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# P97 Sodium-glucose cotransporter 2 inhibitor dapagliflozin: Can this drug undergo oxidative bioactivation?

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Dapagliflozin is part of the antidiabetic drug class sodium-glucose cotransporter 2 inhibitors (SGLT2i). It has been also shown to reduce cardiovascular and kidney disease, regardless of diabetic status, and its usage has recently been extended to some of these applications. [1] However, reports on the risk of idiosyncratic hypersensitivity reactions warrants further investigations about the safety of this drug. [2]

The formation of phenolic metabolites from Dapagliflozin led us to investigate its ability to afford quinoid reactive metabolites. In fact, quinoid metabolites are toxicological relevant reactive metabolites, stemming not only from their redox cycling, with the concomitant production of reactive oxygen species (ROS), which promotes oxidative damage, but also from their electrophilicity, a property responsible for their ability to react with bionucleophiles forming covalent adducts. [3]

To investigate this hypothesis, we have oxidized the phenolic Dapagliflozin metabolite with tyrosinase (TYR) or Fremy's salt and in human liver microsomes in the presence of bionucleophiles (e.g. *N*-acetyl-*L*-cysteine, cysteine and glutathione). Mass spectrometry (MS)-based methodologies were subsequently used to evidence that Dapagliflozin is bioactivated to quinoid metabolites, which are prone to react with bionucleophiles. The covalent adducts identified might, therefore, act as biomarkers of bioactivation/toxicity of this SGLT2i.

These results represent an important step towards the elucidation of the role of these bioactivation pathways in the onset of toxic events associated with Dapagliflozin. Therefore, we will subsequently use the MS-based methods developed and the synthetic standards prepared to investigate the formation of these adducts in patients on SGLT2i regimens, for reliable risk/benefit estimations of Dapagliflozin-based therapeutic regimens.

**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. We also thank Instituto Politécnico de Lisboa for financial support through program IDI&CA 2021: IPL/2021/SGLT2i-PSP_ESTeSL/BII/3M. Fundação para a Ciência e Tecnologia is also aknowledge for contract CEECIND/02001/2017 (to A.M.M.A). Joint funding from FCT and the COMPETE Program through grant SAICTPAC/0019/2015 and RNEM-LISBOA-01-0145-FEDER-022125 funding are also gratefully acknowledged.

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# P98 Early Detection of T cell Exhaustion by Microcalorimetry

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In cancer immunotherapy, T cells are genetically modified to improve their reactivity towards cancer cells. Eventually, this therapy loses effectiveness due to cellular exhaustion, which is characterized by the loss of effector function of T cells [1]. Cellular exhaustion can occur in tumor microenvironments due to the scarcity of nutrients, such as arginine [2], which are avidly taken up by cancer cells. In clinical routine, cell exhaustion is monitored by flow cytometry through the detection and measurement of exhaustion markers expressed by T cells. This method often provides a late exhaustion detection, leading to a loss in therapy efficacy that ultimately results in tumor growth and metastasis.

The aim of the present work is to achieve an early detection of cellular exhaustion using microcalorimetry as an alternative to flow cytometry. The underlying hypothesis is that metabolic changes associated with stress responses (to which cytometry markers are blind) preceding T cells exhaustion, are reflected by an increase of heat dissipation that is detectable by microcalorimetry. As a first step to test this hypothesis, T cells isolated from blood provided by Instituto Português do Sangue e Transplantação were stimulated with anti-CD3 and anti-CD28 antibodies in arginine-rich medium and subsequently monitored by calorimetry. A control experiment was also performed with unstimulated cells from the same batch. The obtained results showed that power dissipation is ca. 3× larger for the stimulated than for unstimulated T cells (**Figure 1**). According to the working hypothesis, heat release by stimulated cells should be even larger in environments where exhaustion is expected to be promoted. To test this assumption, experiments in arginine-deficient media are on the way where proliferation and exhaustion are monitored in parallel by flow cytometry microcalorimetry. If the concept is proved, then calorimetric results will have the potential to provide an early marker of T cell exhaustion compared to flow cytometry.

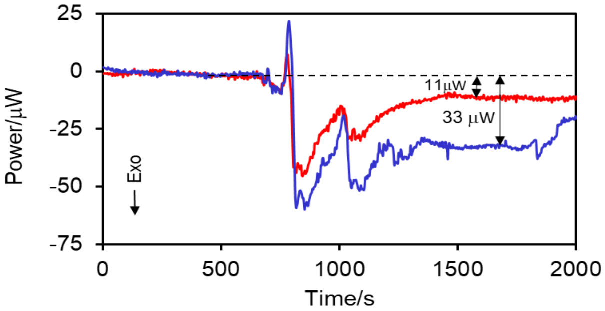

**Figure 1.** Power dissipation by unstimulated (red) and stimulated (blue) T cells, monitored by microcalorimetry. T cells ($1\times10^6$ cells/mL) were introduced into the microcalorimeter after ca. 700 s.

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# P99 Synthesis of potentially bioactive 1,2,3-triazole-containing nucleoside and nucleotide analogs based on D-glucuronamide moieties

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Synthetic nucleosides, nucleotides and their analogs or mimetics have occupied an important place in medicinal chemistry, with a number of compounds in clinical use to treat various types of cancers and viral infections [1]. These groups of molecules are prompted to interfere with nucleos(t)ide-dependent biological events that are crucial for the progress of various diseases [1]. The antimicrobial potential of synthetic and natural nucleos(t)ides has also been well documented [2]. Major issues associated with their clinical use include their low bioavailability and the emergence of chemotherapeutic resistance [1a]. The design and synthesis of novel bioactive nucleoside/nucleotide-like structures that may overcome these limitations, potentiate alternative mechanisms of action and open new therapeutic opportunities is of significant interest.

In this context, we report herein on the synthesis of a variety of nucleoside, nucleotide and sugar diphosphate analogs/mimetics constructed on D-glucuronamide templates, which are rather unusual glycosyl units in nucleoside chemistry, and comprising a 1,2,3-triazole moiety. The triazole unit was envisaged as a surrogate of a nucleobase or as a potential neutral and rather stable surrogate of a phosphate group when combined with other moieties such as phosphonate or amide to establish new potential neutral diphosphate group mimetics. The synthetic methodologies used azido pyranoses and D-glucofuranuronolactone as precursors and employed key steps such as azide-alkyne 1,3-dipolar cycloaddition, *N*-glycosylation, or Arbuzov reaction.

Some compounds were subjected to antibacterial evaluation, from which one showed potent effect against the Gram-positive bacterial pathogen *Streptococcus pneumoniae*, with an activity higher than that of a standard antibiotic, thus tuning it a promising lead molecule for further investigations.

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# P100 Sodium alginate hydrogels loaded with ibuprofen for articular cartilage repair

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This study aimed to develop hydrogels based on sodium alginate for cartilage replacement and to evaluate the effect of the addition of graphene oxide on the material's properties. It was also investigated the possibility of using it as a carrier of an anti-inflammatory (ibuprofen). Hydrogels were prepared with sodium alginate, methacrylic anhydride and a photoinitiator and submitted to a double crosslinking procedure, first by exposure to UV radiation followed by immersion in $CaCl_2$ solution (SAM hydrogels). GO hydrogels were obtained by adding 0.3%(w/v) graphene oxide to the prepared mixture, following a similar procedure. The results demonstrated that graphene oxide affected significantly several properties of the SAM hydrogels:

- Lead to a lower equilibrium water content (decreased from 87.1 ± 2.6% to 81.1 ± 2.7%);
- Increased the Young's modulus and the ultimate tensile strength by 128% and 137%, respectively;
- Enhanced the hydrophilic character (water contact angle decreases from 33.8º ± 6.0º to ~0).

The frictional properties of SAM and GO hydrogels were investigated under different loads and lubricants. In general, the average friction coefficient slightly decreased for SAM hydrogels by increasing the load from 0.32 MPa to 0.47 MPa. The addition of graphene oxide increased friction and wear due to changes induced in the hydrogels' microstructure. It also showed a dependence on lubricant's nature. Lower friction coefficients were obtained in synovial fluid compared to PBS, due to the liquid's viscosity (10x superior for the former), and the presence of biomolecules that enhance lubrication. Evaluation of the material's degradation in PBS showed that GO hydrogels were severely affected after 3 days, losing about 90% of their mass, in contrast with SAM which only lost 4%. Therefore, SAM hydrogels were chosen to be loaded with the anti-inflammatory. A sustained drug-release profile was observed during 72 h, revealing the material's ability to serve as a platform for the local delivery of ibuprofen in the post-operatory period. The drug-loaded and non-loaded SAM hydrogels were tested regarding biocompatibility. Samples revealed to be non-irritating and non-cytotoxic, but the presence of ibuprofen led to minor toxicity.

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# P101 New ruthenium-antibiotic conjugates as potential bifunctional anticancer agents

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Cancer is a leading cause of death, with high morbidity rates and strong economic impact worldwide. Only in 2020, more than 19 M new cases of cancer were diagnosed, occurring 10 M deaths, and costing US$ 1.16 trillion globally. While the World Health Organization estimates a 47% rise of cancer incidence and mortality in the next two decades, most of clinically available treatments still show low efficacy and high adverse effects, impairing a long-term solution for patients with cancer, which urgently claims for novel therapeutic approaches [1].

Cisplatin and analogues are the sole metallodrugs approved for cancer chemotherapy, but they are largely employed to treat more than half of the cases. Despite the severe secondary effects, cisplatin's anticancer proprieties have propelled the scientific community to research for new metal complexes that hold the potential to become more effective metallodrugs. In the past years, our research group has been developing new Ru(II)($\eta^5$-$C_5H_5$) complexes, which have revealed in most of the cases higher cytotoxicity than cisplatin *in vitro* and *in vivo* against several types of cancer (breast, prostate, ovarian, colon) and also antimetastatic activity [2,3].

Despite cancer aetiology being diverse, several tumours are induced by bacterial infections. Each tumour has also a microbiome that influences its progression, metastasis, and drug sensitivity. Moreover, many patients suffer from opportunistic infections caused by lowered immunity induced by cancer itself and conventional chemotherapy [4]. Aiming at developing a more efficient therapeutic approach, herein we conjugated one of our Ru(II)($\eta^5$-$C_5H_5$) complexes 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) of two new ruthenium-antibiotic conjugates containing a linker sensitive to tumour microenvironment for controlled release of each component (cytotoxic complex/antibiotic), that can potentially be used as a multifunctional anticancer agent (**Figure 1**). Their stability in aqueous/ organic solutions was determined over time by UV-vis spectroscopy and will be also discussed.

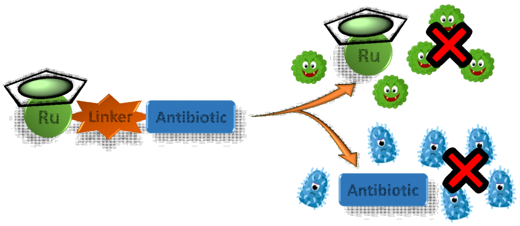

**Figure 1**. Schematic representation and action of the bifunctional ruthenium-antibiotic conjugates.

**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 Ciências e Tecnologias Nucleares is a Research Unit funded by FCT through project UID/Multi/04349/2020. This work was also funded by FCT through project PTDC/QUI-QIN/0146/2020. J. F. Machado thanks FCT for his doctoral grant (SFRH/BD/135915/2018). 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 and 2020/02383/CEECIND, respectively.

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# P102 New Purine Nucleosides as Potential Copper Chelators and Cholinesterase Inhibitors

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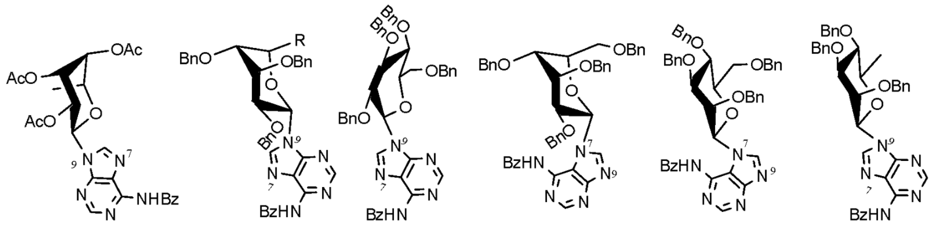
Alzheimer's disease (AD) is a neurodegenerative pathology that is characterized by multiple factors, one of them being the progressive decline of the level of the neurotransmitter acetylcholine [1,2]. Currently, there is no efficient treatment for AD, however it is possible to relieve its symptoms, in its early stages, by using acetylcholinesterase inhibitors. Although this is a merely symptomatic treatment, recent studies suggest that the long-term use of these drugs might lead to disease modifying benefits [3]. Some transition metals, such as $Cu^{2+}$, play a crucial role in the regulation of neuronal functions, existing statistical support showing that serum copper levels were significantly higher in AD patients than in controls [4]. Furthermore, these ions were already found in high concentration in some tumors [5]. In this context, mannosylpurines synthesized in our group showed a potent antitumor activity and a potent butyrylcholinesterase inhibition [6,7]. Inspired by these previous studies, we now present the synthesis of new mannosyl and rhamnosylpurines, which potential as copper chelators and as cholinesterase inhibitors will be disclosed.



1 2 $R=CH_2OBn$ 3 4 5 6
7 $R=CH_3$

**Figure 1**. Structure of some studied mannosyl and rhamnosylpurines.

**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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# P103 New Co(III)($\eta^5$-$C_5H_5$) organometallic complexes for potential application in cancer therapy

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Cancer ranks as a leading cause of death and a burden in society, with 19 million new cases and 10 million deaths worldwide in 2020 [1]. Platinum metallodrugs, such as cisplatin, carboplatin and oxaliplatin, are among the most used anticancer chemotherapeutics. Nonetheless, they show limited efficacy, acquired drug resistance, and severe side effects. Therefore, there is an urgent need of alternative therapeutic approaches. Within this, one important strategy is based on designing new complexes containing endogenous metals, which may lead to lower systemic toxicity than conventional metallodrugs and reach specific biological targets more easily. Cobalt is an essential element for life, playing a key-role in several biological processes of the human body. Inorganic complexes of cobalt have shown promising therapeutic proprieties, yet the anticancer potential of Co(III) organometallic complexes remains scarcely studied and exploited [2].

Herein, we report the synthesis and structural characterization (NMR, FT-IR and UV-Vis) of a new family of organometallic Co(III)($\eta^5$-$C_5H_5$) complexes. The cytotoxicity was determined *in vitro* by the MTS assay in colorectal, ovarian and breast human cancer cell lines and in healthy fibroblasts. The cellular internalization was studied by ICP-AES. The determination of cell death mechanism and ROS production will be presented and discussed as well.

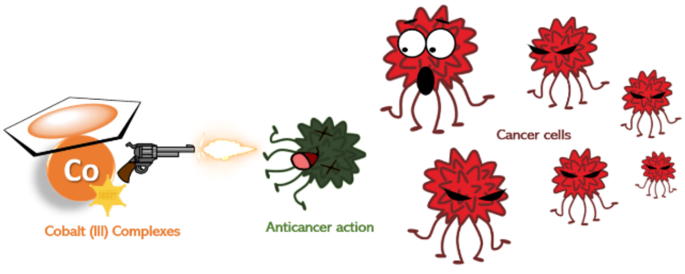

**Figure 1**. Illustration of Co(III)($\eta^5$-$C_5H_5$) complexes killing cancer cells.

**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. Financed by Fundação para a Ciência e a Tecnologia, I.P./MCTES through national funds (PIDDAC) - UIDB/00100/2020 (CQE), LA/P/0056/2020 (IMS), UID/Multi/04349/ 2020 (C2TN), UIDP/04378/2020 and UIDB/04378/2020 (UCIBIO), LA/P/0140/2020 (i4HB), and project PTDC/QUI-QIN/0146/2020. J. D. and S. C. thank FCT for the projects PTDC/QUI-QIN/0146/2020 (Fciencia.ID) and PTDC/BII-BIO/31158/2017 (NOVA.id.FCT), respectively. J. F. M. thanks FCT for his doctoral grant (SFRH/BD/135915/2018). T. M. thanks FCT for CEECIND 2017 Initiative for the project CEECIND/00630/2017 (acknowledging FCT, as well as POPH and FSE-European Social Fund).

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# P104 Development of a monosubstituted 2,2'-bipyridine ligand for a new promising anticancer ruthenium complex

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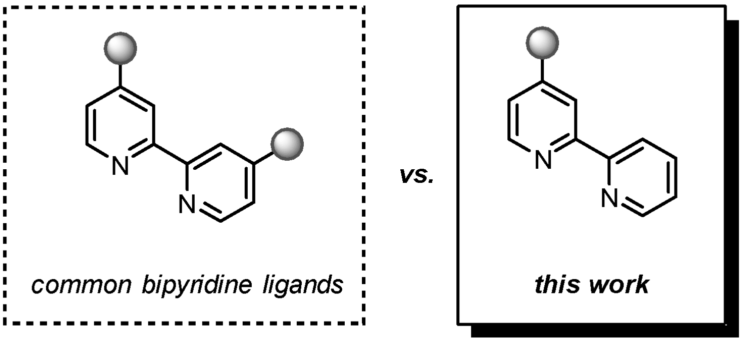
Bidentate chelating ligands containing nitrogen as donor atoms have been used for designing inorganic and organometallic complexes with several medicinal applications[1-2]. In particular, symmetric 2,2'-bipyridine ligands [3] have attracted attention as chemotherapeutics in cancer treatment [4]. Among them, the ruthenium complex with 2,2'-bipyridine $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(2,2'\text{-bipyridine})][CF_3SO_3]$ has emerged as a promising anticancer agent, due to its high antitumoral activity [4]. Nonetheless, metal complexes containing monosubstituted 2,2'-bipyridines as prospective anticancer metallodrugs remains underexploited, mostly due to sparce commercially available options.
Herein, we disclose the synthesis, structural characterization (NMR, UV-visible, FT-IR), and biological evaluation of an unexplored 4-monosubstituted 2,2'-bipyridine, as well as of a ruthenium cyclopentadienyl complex containing this ligand. The stability of the complex in solution was evaluated over time by UV-visible spectroscopy. The anticancer potential of the two compounds was determined *in vitro* in a human breast cancer cell line.



**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 Ciências e Tecnologias Nucleares is a Research Unit funded by FCT through project UID/Multi/04349/2020. This work was also funded by FCT through project PTDC/QUI-QIN/0146/2020. J.F.M. thanks FCT for his doctoral grant (SFRH/BD/135915/2018). J.A.S.C. and T.S.M. thank FCT for Scientific Employment Stimulus 2020/02383/CEECIND and CEECIND/00630/2017, respectively.

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# P105 Synthesis of new glycoconjugates with potential against infections caused by multidrug-resistant Gram-negative bacteria

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Antimicrobial resistance is a serious public health concern threatening to cause 10 million deaths annually until 2050 if no effective solutions are found in the meantime [1]. A recent study developed by the Carbohydrate Chemistry Group of CQE showed that dodecyl deoxy glycosides act on phosphatidylethanolamine (PE)-enriched membranes of Gram-positive bacteria, leading to bacterial cell lysis, with acceptable toxicity in human cell lines. However, these compounds are not active against Gram-negative strains: despite their ability to cause the rupture of their inner membrane, they cannot get through the outer membrane to reach the target [2]. The present work focuses on the synthesis of optimized dodecyl 4,6-dideoxy-α-D-*xylo*-hexopyranoside analogues with improved molecular affinity for PE and, ultimately, enhanced bactericidal activity against the most problematic multidrug-resistant Gram-negative bacterial strains [3] when combined with adjuvant agents that allow glycoside passage through the outer membrane.

To ensure that the synthesis of a compound library is as efficacious as possible, we have optimised the synthetic route toward the lead compound, which was successfully accessed in fewer synthetic steps and higher overall yield compared to the originally described procedure [4]. The synthesis of the first lead analogue, 8-phenyloctyl 4,6-dideoxy-α-D-*xylo*-hexopyranoside, is currently ongoing, and the already accomplished synthetic steps will be explored in this communication. Importantly, despite the therapeutic potential of alkyl glycosides as antibiotics, there is still no information about their pharmacokinetic profile with regard to the affinity toward human serum albumin (HSA) - the primary transport and reservoir protein in the bloodstream. Therefore, the binding affinity of the synthesized compounds for HSA will be assessed through fluorescence spectroscopy in order to predict their potential to be delivered to target tissues through blood circulation.

**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. A.M. Matos thanks CQE for her PhD Scientific Researcher contract. T.S. Morais thanks FCT, as well as POPH and FSE-European Social Fund for CEECIND 2017 Initiative for the project CEECIND/00630/2017.

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# P106 Bar Adsorptive Microextraction - A novel green sample preparation perspective in doping control

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During the development and implementation of analytical methodologies, the main objective is mainly to obtain irrefutable technical-scientific results, complying with strict and strong legal requirements.

Due to the high complexity of the biological samples (e.g., urine), the respective handling or preparation is a very relevant task during the development of methods, allowing the analytical enrichment at the trace level, as well as the elimination of potential interferences, both decisive particularly in the correct identification of illicit substances.

In the last decade, bar adsorptive microextraction (BAµE) has emerged as a new perspective in sample preparation. 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. BAµE operates in static mode and under floating sampling technology, using solid or polymeric materials with adequate physicochemical properties, achieving excellent efficiency for both polar and non-polar target substances. In addition, BAµE includes several advantages such as high sensitivity, high selectivity of the sorbent phases, excellent efficiency, miniaturization suitable for the combination with the analytical systems and, in addition to low cost, it is an ecological approach. In this sense, BAµE seems to be an excellent alternative as a sample preparation technology in doping and forensic contexts. [1-4]

The present contribution aims to discuss the high analytical potential of the BAµE technique in doping control, as an unconventional approach to sample preparation for enrichment purposes, while other more common ones may show analytical limitations.

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# P107 Synthesis of novel bisquinolizidine derivatives from bio renewable resources

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Bisquinolizidine alkaloids, such as (+)-lupanine and (-)-sparteine, are found in several plants of the subfamily *Faboideae* including the genus *Lupinus*. These molecules are characterized by a common chiral bispidine core and possess a variety of biological activities, from antiarrhythmic and oxytocic properties to a partial agonist of the nicotinic acetylcholine receptor [1,2]. Our group have been developing methods for the sustainable isolation of these alkaloids [3]. Currently, our research interests include developing methodologies for the functionalization of bisquinolizidine alkaloids for medicinal chemistry applications. In this work, we present a convenient synthesis of 17-substituted lupanine derivatives through addition of Grignard reagents to iminium ion formed from lupanine (**Figure 1**).

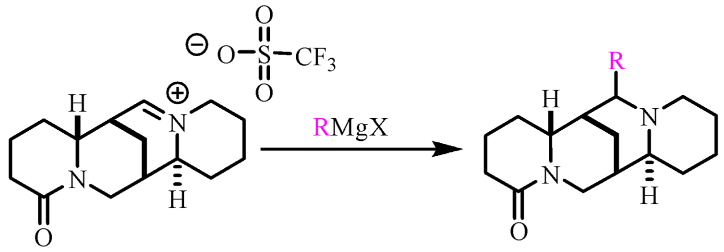

**Figure 1**. Reaction scheme of the addition of Grignard reagents.

**Acknowledgments:** We thank the FCT for financial support (UIDB/04138/2020 and UIDP/04138/2020), COMPETE Programme (SAICTPAC/0019/2015) and PTDC/QUI-QOR/1786/2021. The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996. J.A.S.C. thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND. 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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# P108 Application of bar adsorptive micro-extraction for the identification of cocaine and its metabolites in doping control

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Stimulants present in the World Anti-Doping Agency (WADA) list of prohibited methods and substances in sport, is one of the classes with higher percent of positive tests. Cocaine is one of the most consumed stimulants and it's used to enhance the athlete's performance. This drug has a very rapid metabolic disposition, forming two major metabolites, ecgonine methyl ester and benzoylecgonine. Besides these two, the consume of cocaine combined with alcohol forms another metabolite, the cocaethylene. [1-2]

Over the last decade a new sample preparation technique has been introduced, bar adsorptive microextraction (BAµE), as a new environmentally friendly technique. It consists in a small analytical device with an appropriate geometry, coated with suitable sorbent, that operates under floating technology, to retain the target analytes. This approach showed to be suitable for polar and nonpolar substances, reaching high sensitivity, selectivity, and efficiency. BAµE is a greener alternative and a very cost-effective approach to the common sample preparation methodologies, such as liquid-liquid extraction and solid-phase extraction. [3-5]

The present contribution proposes a novel methodology for trace analysis of cocaine and its metabolites in urine samples, using BAµE combined with gas chromatography coupled to mass spectrometry (GC-MS), in compliance with WADA's requirements in doping control.

**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 also thanks to Instituto Português do Desporto e Juventude, I.P. (IPDJ).

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# P109 A sneak peek into the toxicity of an imidazolium ionic liquid provided the worm *Caenorhabditis elegans*

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Ionic liquids (ILs) can be defined as materials that are composed of cations and anions which melt at or below 100 °C. ILs application in the chemical industry increased largely due to their tunable properties, as a result of the number of possible combinations of a cation and anion, making it theoretically possible to synthesize an IL targeted for a specific application or property [1].

The awareness on the threat of aquatic and terrestrial environments contamination by these compounds has increased over the years. In fact, recent studies have detected ILs in wastewater effluents and sediments [2]. In this context, the (eco)toxicological risks of ILs to human health and ecosystems should be investigated towards a comprehensive hazard assessment. This preliminary study was designed under this scientific challenge, aiming to improve the knowledge on the potential toxicity of an imidazolium ionic liquid (1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][OTf]) using a widely recognized model (*Caenorhabditis elegans*) in the human health sciences research, which has also been applied in the ecotoxicology investigative context [3]. Three independent experiments with *C. elegans* were carried out, comprising its short-term exposure (1 hour) to a range of exposure levels (0.01, 0.1, 1, 10 and 15 mg/mL) of [emim][OTf]. Then, survival was assessed 24 and 48 hours upon exposure, while effects on development were evaluated right after the exposure and then at 48 hours. Locomotion behavioral alterations were additionally examined. While no significant effects on survival were detected, findings suggest an impairment of the worms' development upon exposure to the two highest levels of [emim][OTf] tested. It should be highlighted that the reported compromise of the worms' development was noticed both upon the short-time exposure (1 hour) and after the 48 hours of worms' placement in clean plates. This could have possibly allowed the recovery of the worms, which was not the case, pointing out long lasting effects of this IL. Although behavior was not strictly assessed in this study yet, changes on *C. elegans* locomotion behavior were noticed right after the short-term exposure with worms exhibiting an omega turn behavior and a reduced activity (*i.e.* decreased body bending or paralyzed worms). Even though preliminary, these results raise concerns on the toxicity of a highly used class of ILs (the imidazolium), pointing out the need of more research on their biological effects.

**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. ILGerants is a project funded by FCT through project LISBOA-01-0145-FEDER-032066 + PTDC/EQU-EQU/32066/2017. P.Pereira is funded by national funds through FCT, under the Scientific Employment Stimulus (Individual Call) [CEECIND/01144/2017].

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SUSChem

# P110 Application of design of experiments in supercritical $CO_2$ extraction of compounds from rice bran. Optimization and modelling

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The valorization and reuse of biomass with natural antioxidants is a current topic because these compounds can capture free radicals, resulting from the most diverse origins including those from pollutants. The compounds present in rice bran oil function as natural antioxidants, providing it with greater resistance to oxidation or deterioration. After corn, rice is the second most produced cereal worldwide, producing about 730 million tons (Mt) annually. In Europe, rice production reaches 4.4 Mt per year [1].

Using supercritical carbon dioxide extraction, a design of experiments (DoE) was applied for process optimization. Initially, a $2^{4-1}$ two level Fractional Factorial Design was used and the variables pressure, temperature and $CO_2$ flow rate, for yield responses, flavonoids and total polyphenols were identified as the significant experimental factors. Consequently, Central Composite Design (CCD) was applied to analyze the effects of the significant variables on the response, and quadratic surfaces to optimize those responses were generated.

Yields were obtained between 5.07 and 6.91% in relation to the initial mass of charge in the extractor, flavonoid values between 1314.3±79.8 to 1902.9±105.6 (µmol EC/g ext) and for total polyphenols between 55.35±1.12 to 73.41±1.55 (mmol EAG/g ext), which were in excellent agreement with those predicted from the CCD model.

Finally, modelling of the experimental data of the extraction of the oil from rice bran were performed using three mathematical models [2], based on differential mass balances. In all the internal mass transfer coefficient ($k_s$) have been found to change with pressure and temperature.

The elimination of organic solvents in the process, using environmentally sustainable solvents, supercritical $CO_2$, as well as the values obtained from the responses in the process allows good expectations for the application of a technology considered green.

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# P111 Seasonal variation of nutrient levels at the international Tagus River – Metrological assessment

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Policies for the protection of environmental water resources are based on the regular monitoring of their health. This monitoring must be of adequate quality and produce objective information on contamination levels and their trends. The objectivity of analytical information is achieved by evaluating the uncertainty of the measurement of contaminants and their variation [1,2]. The characterization of vast environmental compartments is affected by the seasonality of environmental systems, the heterogeneity of their composition and the representativeness of the sampling.

The international Tagus is the portion of the river that serves as the border between Portugal and Spain and deserves regular monitoring of its environmental health, since the daily flows that satisfy the interests of Spanish hydroelectric plants often do not correspond to those defined, presenting seasonal variations in the nutrient content of the international Tagus. When this happens, the Tagus river reach the Portuguese territory already polluted having large amounts of sludge caused by irregular amounts of nutrients.

This work involves the first assessment, with known uncertainty, of seasonal variations in the content of nitrite, nitrate, phosphate and sulfate in the waters of the international Tagus River in order to obtain objective and binding information on the health of this river. Samples collected at known GPS coordinates will be analyzed by validated methods based on ion chromatography.

Innovative and user-friendly sampling uncertainty assessment tools are used, which make the work particularly useful for the quality control laboratories.

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# P112 Bar adsorptive microextraction (BAμE) – Fast, effective, and easy to use sampling devices for screening synthetic cannabinoids in oral fluids

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The last decade has seen an increase of new psychoactive substances (NPS) that were widely spread through "smart shops" and over the web [1]. In Europe, synthetic cannabinoids are one of most diffused NPS, being illegally marketed as legal alternatives to cannabis. Since 2008, more than 209 new synthetic cannabinoids were detected in a wide range of different products. Many toxicity symptoms were associated with the consumption of these NPS, resulting in some cases of fatal intoxications [2]. For this reason, there is a need for the development of innovative analytical approaches to allow an effective monitoring of these drugs in biological matrices, using non-invasive sampling, *e.g.*, oral fluids. This work presents the development, optimization, validation, and application of a novel methodology, based on bar adsorptive microextraction (BAμE) [3], followed by microliquid desorption using only 100 μL of solvent, in combination with high performance liquid chromatography with diode array detection for monitoring eight synthetic cannabinoids (AM-694, SGT-25, MAM-2201, 5F-UR-144, JWH-018, JWH-122, UR-144 and AKB-48) in oral fluids. This new approach presents excellent extraction yields (87.9 – 100.5 %) using two spiking levels (50.0 and 300.0 μg $L^{-1}$). The limits of detection were between 2.0 and 5.0 μg $L^{-1}$. The optimized methodology was fully validated in the linear range of 20.0 and 2000.0 μg $L^{-1}$ ($r^2 > 0.99$, RSD < 15 %). The developed method also presented good intraday ($n = 6$) and interday ($n = 6$, five consecutive days) trueness (bias < 11 %) and precision (RSD < 10 %) using three spiking levels (50.0, 300.0 and 1000.0 μg $L^{-1}$). In short, the proposed analytical approach, using miniaturized sampling devices, proved to be a suitable eco-user-friendly methodology to monitor these synthetic cannabinoids in oral fluids.

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# P113 Quality assessment of the oil spill identification performed by different methods

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Oil spills and refined products are a widespread problem and lead to high costs for society at economic and environmental levels. Thus, chemical analysis, performed on samples collected in the spill and suspected source(s) of its origin, has been a valuable support for judicial investigations. Oil spill identification is based on the distinct relative content of hydrocarbons in crude oil and its derivatives, namely fingerprint, allowing the differentiation among their types and origins. The applicable analytical methodologies use Gas Chromatography-Mass Spectrometry (GC-MS) to provide an extensive characterization of the hydrocarbon content of the oil samples. To characterize the fingerprint of each sample are used abundance ratios between chromatographic signals of specific components, *i.e.*, diagnostic ratios (DR). The DR observed in the different samples are then compared using conventional or multivariate statistical methods. The equivalence between a set of relevant DR, observed for the spill and suspected source samples, indicates sample composition equivalence and allows the identification of the spill origin. The most common approaches to compare DR observed in a spill and suspected source samples are based on Student's *t* statistics and a maximum relative difference of 14% [1-3]. The Nordtest method suggests the triplicate analysis of samples and the comparison of DR using Student's *t* statistics (S-t), which assumes that the probability distributions of DR follow the normal distribution [1]. In contrast, the CEN 15522-2 methodology, revised in 2020 and submitted for publication as a reference standard (prEN 15522-2), suggests the analysis of duplicate samples and uses a single criterion (SC) for evaluating DR equivalence [2,3]. This approach for DR comparison relies on empirical knowledge that experts have acquired over the years, assuming a most expectable dispersion (relative standard deviation of 5%). However, the chromatographic signals that define the DR have specific dispersion and correlation, responsible for deviations to the normality of their probability distributions [4]. Therefore, if inadequate assumptions or approximations are considered, erroneous assessments can be made about the equivalence of DR and, consequently, about the fingerprints equivalence of compared samples. The development of approaches for results interpretation based on statistical methods that better describe the reality of the variables under study is essential to ensure identification quality. This work compares the two mentioned common approaches for the assessment of DR equivalence, *i.e.*, S-t and SC, with a developed alternative approach based on the accurate simulation of correlated chromatographic signals using the Monte Carlo Method (MCM). The comparison among the three approaches consisted in defining criteria for DR comparison and quantifying the probability of true acceptance of compositional equivalence between two samples (*i.e.*, total risk).

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# P114 Nanoporous materials development: synthesis, characterization and adsorption/separation of gases

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One of the byproducts formed during biodiesel production is glycerol, which can be used as an activated carbon precursor, instead of being discarded [1]. In this work, crude glycerol was carbonized in the presence of $H_2SO_4$[2], activated with $CH_3COOK$ in different ratios and finally, characterized using low-temperature $N_2$ adsorption, $pH_{PZC}$, density, FTIR, SEM and elemental analysis. The glycerol-activated carbons present high surface area (520-1115 $m^2g^{-1}$) and pore volume (0.06-0.42 $cm^3g^{-1}$).
Since $CO_2$ and $CH_4$ are two of the more abundant greenhouse gases in the atmosphere, getting ways to capture them is necessary to reduce their consequences [3]. In this context, the glycerol-activated carbons were used to study their $CO_2$ and $CH_4$ adsorption-separation capacity. Based on the isotherms obtained, the selectivity of $CO_2$ over $CH_4$ was calculated [4]. Additionally, all the glycerol-activated carbons exhibited higher adsorption capacity of $CO_2$ over $CH_4$. Their $CO_2$ adsorption capacity were up to 3.40-4.13 mmol/g and their $CO_2/CH_4$ adsorption selectivity were in the range of 2.3-10.7. Hence, glycerol, a low cost by-product of biodiesel production, can be transformed in a valuable material with promising properties for adsorption-separation of $CO_2/CH_4$.

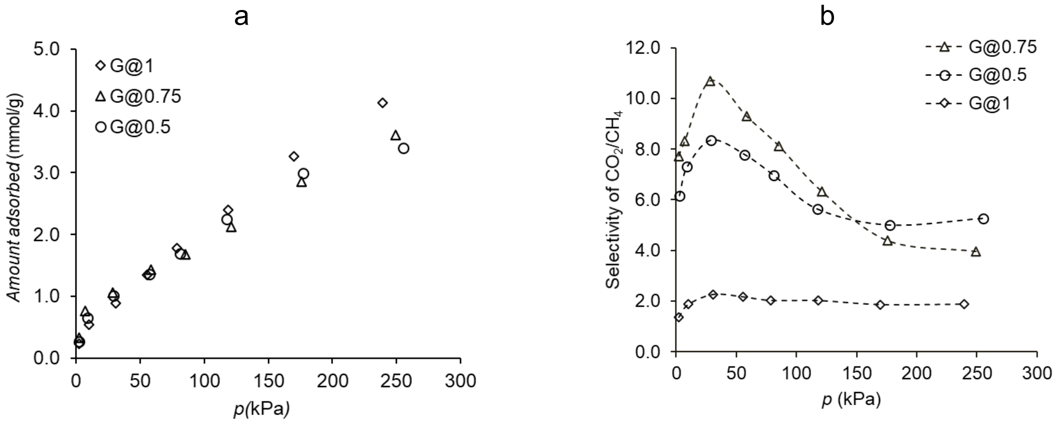

**Figure 1**. (a) Adsorption isotherms $CO_2$ (b) Selectivity of $CO_2$ over $CH_4$ for the synthesized materials.

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# P115 Can plastic environmental threat be a matter of size? Lessons learned from multi-biomarkers in common carp juveniles

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Aquatic organisms have been naturally exposed to an increasing global problem posed by plastic pollution. However, we still lack documenting its ecological risks and the changes induced by plastics in many organisms, particular in those for human consumption like fish. This work addressed the impact caused by different sizes of polyethylene (PE) plastics in the common carp (*Cyprinus carpio* L.) through an evaluation of its multi-biomarker responses [1].

Fish (n=30) were divided and acclimatized in four tanks (control + 3 treatments), monitoring the physicochemical properties of the water. Each treatment consisted on exposing the fish to the same nominal concentration (100 mg/L) to PE macro- (MaPs), micro- (MPs), and nanoplastics (NPs) for a period of 15 days, maintaining the plastic concentration in each treatment by adding the respective PE-containing solution in the daily-renewed water for the tanks. After exposure, alterations in the fish health status were evaluated in each treatment compared to the control, using a multi-biomarker approach. The data collected included hematological, biochemical and immune parameters, antioxidants and cholinesterase activity, in addition to the histological analysis of the liver and intestine tissues.

Visual inspection of the fish depicted the death of two and one individuals after the exposure to NPs and MPs, respectively, whereas all fish survived in MaPs and control groups. Most of the measured hematological indices significantly decreased ($P < 0.05$) after exposure to the different sizes of PE plastics. Higher levels of enzymes (LDH, AST, ALT, CK, and ALP) were found in the blood, which were indicative of cell membrane damage. Our results indicated that the activities of serum enzymes as a response of the fish to the presence of plastics were enhanced with the decreasing size of the PE particles (NPS > MPs > MaPs). The activities of SOD and CAT significantly decreased ($P < 0.05$) after exposure to MPs and NPs, as compared to the control group, whereas no significant differences ($P > 0.05$) were observed in the MaPs treatment. The levels of ChE and lysozyme also decreased with the decreasing size of PE plastics (NPS < MPs < MaPs). Moreover, changes in erythrocytes increased with the decreasing size of particles (NPs > MPs > MaPs) compared to the control. As to the histological analysis, severe damage in the liver tissue was caused by all sizes of PE particles, depicting degeneration of hepatic structures and necrotic hepatocytes. Similarly, damage in the intestinal tissue was observed too. Our findings suggest that fish responses are comparable to those induced by other contaminants in the environment, yet augmented proportionally to the decreasing size of PE particles. A synergistic effect resulting from the individual impact of plastics penetration in the circulatory system, bursting biochemical responses and lesions in tissues might explain the larger impact of NPs as compared to MPs and/or MaPs.

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# P116 MONITOOL – A European consortium for improving metal monitoring of transitional and coastal waters

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A broad geographical study on priority metals by spot measurements and passive samplers was carried out in the project MONITOOL (EAPA 565/2016; https://www.monitoolproject.eu) The project proposed the validation for using passive sampling devices, Diffusive Gradients in Thin-films (DGT) in a regulatory context, taking advantage that labile metal concentrations are a recognized proxy to the potential bioavailable fraction rather than its total dissolved concentrations (discrete water samples filtered through a 0.45 µm membrane). Therefore, MONITOOL aimed at establishing a robust database of dissolved and labile metal concentrations in transitional and coastal waters for adapting the existing Environmental Quality Standards (EQS) for passive sampling devices (EQS-DGT) to improve and facilitate the chemical status assessment of water bodies.

The Canary Islands to the North Sea, including the western Mediterranean Sea, were surveyed (n=28). DGT-holders were deployed at ≈0.5 m depth below the surface and retrieved from the water between 2 to 7 days after deployment (≈250 DGT). All partners collected over 500 discrete samples of water concurrently with the deployment of DGT from the same batch. Filtered and acidified water samples were analyzed for total dissolved concentrations of Cd, Pb and Ni by ICP-MS, along with the DGT, whereas the labile fraction of Cd and Pb was analyzed by voltammetry [1-4].

Based on the statistical relationships between labile DGT and spot sampling concentrations, it was possible to propose EQS-DGT for Cd, Ni and Pb. Furthermore, protocols for the deployment of DGT were also created [4] with the aim of being uniformly used by State Members in investigative and monitoring programmes such as the EU Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD). However, the dissolved concentrations found for the priority metal ions were, in almost all locations, below the EU WFD’s guideline levels for non-inland water bodies.

The MONITOOL project has been recently extended and it will be devoted to sampling new relevant regions specifically to address shortfalls in metal concentrations from the original sampling campaigns. The need to provide data at higher levels of metal concentration for validation of EQS-DGT modelling can facilitate the translation of DGT applications to a wide potential user group. This will lead to an effective communication plan towards an array of stakeholder types, while developing/improving materials such as policy recommendations and protocols for methods will facilitate that communication.

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# P117 Remediation of soils contaminated with total petroleum hydrocarbons through washing with solutions surfactant's solutions

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The soil fulfils vital functions for life on Earth and it is urgent to protect it from all sources of contamination. However, with the increase in industrial activity, environmental liabilities arising from petroleum by-products have been found. The status of local soil contamination in Europe estimates the occurrence of about 2.8 million potentially contaminated sites, with more than 650 thousand contaminated sites already registered in national inventories [1]. Biological, chemical, and thermal remediation techniques have been developed to remove/reduce or immobilize pollutants. Ex-situ soil washing is one of the promising technologies to concentrate contaminants, allowing soil cleaning and the reuse of extracted oils.

In this work, an ex-situ soil washing process using two surfactants, sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan monooleate (Tween 80), was tested in the decontamination of an artificially contaminated sandy soil with burnt oil. The choice of surfactants was based on their physicochemical characteristics, with preference for surfactants that have a low critical micelle concentration, low toxicity, high hydrophilic-lipophilic balance value and low cost. An optimization of the washing conditions was carried out, including a kinetic study of experimental parameters, such as stirring speed, liquid-solid ratio, number of washing stages, concentration of surfactant, effecting soil washing was carried out. An TPH removal efficiency of (81±3)% was obtained with Tween 80 after 5 hours of washing and (91±3)% with SDS after 2 hours at 200rpm on an orbital shaker and L/S ratio of 15. The performance of using microfoams of both surfactants was also evaluated, observing an improvement of about 10% for the SDS. The reuse of the washing solution was tested and promising results were obtained for SDS. Finally, the safe disposal of the washing solution was also tested through the use of activated carbon.

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# P118 Studying the impact of seasonal changes and plant activity in the production of methylmercury in saltmarsh sediments using mercury stable isotope techniques

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Mercury (Hg) is a recognized global pollutant and its impact in ecosystems can have dramatic effects. Previous studies have reported highly Hg contaminated areas in Tagus estuary, which makes of extreme importance to understand Hg biogeochemical cycle at a local scale. In saltmarshes, recent studies have suggested that the rhizosphere of halophyte plants play an import role in Hg speciation, more specifically in the Hg methylation to form methylmercury (MMHg), it's most toxic form.

Trough out the seasons, we evaluated Hg and MMHg natural concentrations and used stable isotope techniques to determine methylation ($K_M$) and demethylation rates ($K_D$) in saltmarsh sediments. Our aim was to evaluate the impact of plants on the MMHg budget in saltmarshes and understand the impact of seasonal changes in the MMHg production. Two saltmarshes in Tagus estuary will be used as study areas: one located in a Hg contaminated area of the estuary (Rosário - ROS) and another used as a reference site (Alcochete - ALC), located inside a natural reserve. Mercury contents varied between 0.13 and 1.14 μg $g^{-1}$ in ALC and between 0.05 and 4.65 μg $g^{-1}$ in ROS. These environments also presented significant MMHg concentrations, varied between 0.4 and 19.0 ng $g^{-1}$ in ALC and between 0.1 and 131.5 ng $g^{-1}$ in ROS. The highest MMHg contents were generally recorded in vegetated sediments, which indicates the influence of plant activity in the Hg methylation. Also, in both saltmarshes, the highest MMHg concentrations were recorded during summer, implying that higher temperatures favour MMHg production likely due to higher microbial activity in warmer months. This was also corroborated by the significant increase of $K_M$ during summer with values up to 0.135 $day^{-1}$ and 0.149 $day^{-1}$ respectively in ALC and ROS. Additionally, the elevated $K_D$ (between 1.5 – 13.6 in ALC and 4.9 – 25.7 $day^{-1}$ in ROS) with sligthly changes between seasons and considerably affected by the presence of plants, indicates that demethylation process happens faster than the methylation process. Higher $K_D$ values combined with measured half-life of less than 2 days for MMHg (mostly in ROS sediments) is surprisingly short. In these particular cases, it indicates that MMHg is not persistent in aquatic systems and a constant supply of MMHg is necessary to maintain a steady level of MMHg in sediments, making the formation process important.

These results showed that the use of stable isotope techniques allowed us to understand the importance of the balance between $K_M$ and $K_D$ in the MMHg pool in saltmarsh environments.

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# P119 Nanostructure in 1-alkyl-3-methylimidazolium cations octyl-sulfonate ionic liquid homologous series

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Many biomedical applications and physical-chemical functionalities, such as detergency, surface-activity agency and oil recovery, emerge from the addition and use of sulfonate groups in polymers [1]. In this work, ionic liquids combining 1-alkyl-3-methylimidazolium cations, $[C_nC_1im]^+$, with octyl-sulfonate anions, $[C_8SO_3]^-$, (**Figure 1**) have been studied. This combination enables the analysis of the sulfonate group effects in such ionic liquids, whilst exploring the influence of the increase of alkyl-chain length in the cation. This contribution will be crucial to unravel the nature of the interactions and structure in different ionic compounds containing not only sulfonate groups, but also different sizes of the non-polar domain. To that effect, several analyses, including radial distribution functions, RDF, structure factors, *S(q)* and aggregation analysis, obtained from molecular dynamics (MD) simulations are attained and discussed to its physical meaning [2].

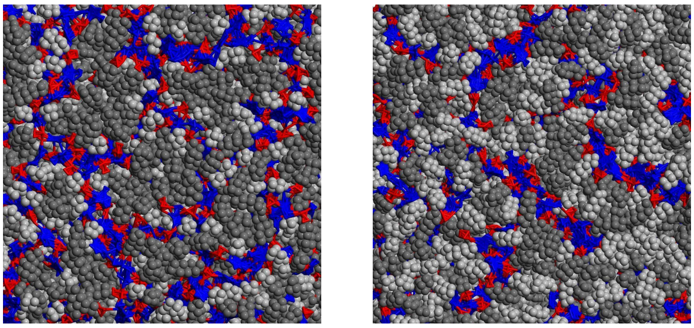

**Figure 1**. Snapshots of the MD simulation box performed at p = 1 bar for $[C_4C_1im][C_8SO_3]$ (left) and $[C_8C_1im][C_8SO_3]$ (right). The blue and red colors depict the polar part of the cations (imidazolium ring) and anions, respectively, and the grey and dark grey colors represent the non-polar alkyl chain of the cations and the anions, respectively.

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# P120 Unprecedented mechanochemical synthesis and heterogenization of a C-scorpionate Au(III) catalyst for microwave-assisted biomass valorization

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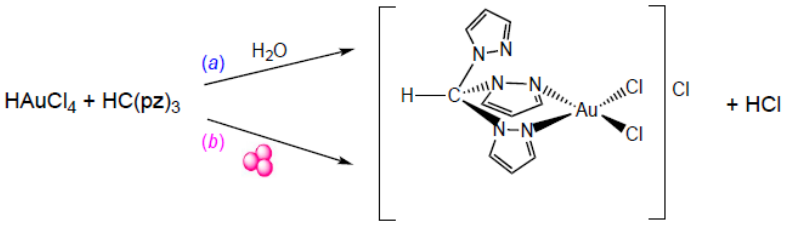
This work presents the microwave-assisted oxidation of biomass-derived substrates, such as glycerol and the furfural derivatives 5-(hydroxymethyl)furfural (HMF) and 5-hydroxymethyl-2-furancarboxylic acid (HFCA), using the C-scorpionate dichloro-gold(III) complex $[AuCl_2(\kappa^2\text{-Tpm})]Cl$ (Tpm = $HCpz_3$; pz = pyrazol-1-yl) as a catalyst, prepared by two different routes (**scheme 1**) and supported on graphene, in solvent-free conditions. The immobilization of $[AuCl_2(\kappa^2\text{-Tpm})]Cl$ on graphene was performed using different methods, e.g., microwave irradiation and liquid assisted grinding.

The prepared hybrid catalysts revealed to be more promising than neat Au(III) complex for the tested microwave-assisted oxidation reactions, leading to higher yields and selectivities for the desired products and allowing an easy separation and recycling. [1]



**Scheme 1**. Synthesis of the C-scorpionate gold(III) complex, $[AuCl_2(\kappa^2\text{-Tpm})]Cl$, in conventional liquid phase (Route a) and by dry mechanochemistry (Route b).[ 1]

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# P121 Electrochemical oxidation of abietanes

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Colophony, a natural resin obtained from coniferous trees, is 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 the antimicrobial, antiviral, antitumoral, and anti-inflammatory activities. Constituents of this resin have a wide range of industrial applications, including synthetic rubbers, adhesives and fragrances. [1,2]
The benzylic oxidation of dehydroabietic acid, an abietane from colophony, and its methyl ester derivative, has been reported using oxidative protocols, such as using Jones reagent [3], Swern oxidation [4] or either using Chromium trioxide in stoichiometric [5] or catalytic quantities. [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 report an electrochemical method for the benzylic oxidation of dehydroabietic acid, an alternative greener protocol for the formation of the benzylic ketone in very good yields using modern electrochemical methods. (**Scheme 1**). Moreover, this method can be applied to the corresponding methyl ester derivative. [7-9]

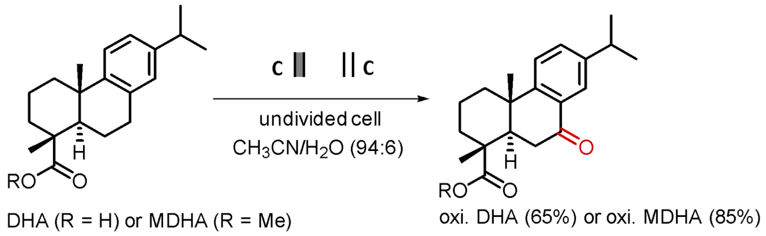

**Figure 1**. Electrochemical oxidation of dehydroabietic acid (DHA) and its methyl ester derivative (MDHA).

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# P122 Electrochemical performance of mixed nickel manganese oxides as charge storage electrodes

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Currently, energy storage devices such as batteries and supercapacitors (SCs) have received great attention in the global energy market. SCs are, typically used for high power, for short periods with a high-rate capability. They can store energy either in the electrical double layer formed in the electrode-electrolyte interface(carbon-carbons SCs) or by fast redox reactions, which occur due to the surface interaction on the active electrode or by the combination of both [1]. For supercapacitors, the design of the electrode architecture can effectively boost the device performances because electrode composition, morphology and structure can influence the electrochemical performances of SCs [2]. Ni oxides have the advantage of reaching a high theoretical specific capacitance, while Mn oxides are low-cost, have several valences and multiple redox reactions [3]. Herein, in this work, we assess the effect of NiOx/MnOx proportion produced via solvothermal reaction, using different precursors, temperatures, and solvents. To evaluate the electrochemical response of the resultant NiOx/MnOx materials, available in powder form after activation, an electrode slurry containing the active carbon must be prepared. To that end, the ink was prepared using standard conditions reported elsewhere [4]. The mixture was coated on Toray Carbon Paper®, used as substrate. Electrochemical tests were performed in 1 M $Na_2SO_4$ and 1 M KOH electrolytes using a three-electrode cell configuration. Cyclic voltammetry was performed at scan rates ranging from 10 mV $s^{-1}$ to 100 mV $s^{-1}$. Galvanostatic charge-discharge curves were obtained at different specific currents. Electrochemical impedance spectroscopy (EIS) was used to further elucidate the electrochemical properties of the best-performing ACs for energy storage applications. EIS was performed by applying a sinusoidal perturbation with 10 mV amplitude in the frequency range from 0.01 to 104 Hz. Cycling stability tests were performed by means of continuous CD at 10 A $g^{-1}$ for 5000 cycles. In 1M KOH electrolyte the NiOx:MnOx (1:3) electrode composite material showed the motivating specific capacitance, with 160 F $g^{-1}$ at 0.5 A $g^{-1}$ and a high coulombic efficiency. The combination of all these techniques revealed insights on the electrochemical properties of the performing electrode materials activated carbons for energy storage applications.

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# P123 Initial studies on novel biocompatible solvents: ChPep from a molecular dynamics perspective

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The investigation on Ionic Liquids (ILs) was trembled when the greenness of these neoteric solvents was challenged and, as a result, ILs configured with substances from a natural origin have emerged as more biocompatible and biodegradable alternatives than their conventional analogues [1], which has prompted deeper research on these bio-based solvents in the recent years. Some of the most studied and applied from this group of ILs are those made-up with the Choline (Ch) cation and Amino-Acid (AA) anions [2,3], which produce a limited number of possible solvents. In this context, our research group has recently proposed the use of peptides (Pep) as anions [4,5], which increments the amount of ChAA ILs that can be configured since combining $x$ AA in peptide chains of $y$ residues returns $x^y$ different anions.

Despite having already been applied [4,5], the study of the nano-segregation of ChPep, and more particularly the effect of employing greater peptides and more complex residues, have not been tackled yet. This work aims to address these issues. To this end, we selected a computational approach for studying a set of ChPep using (i) classical Molecular Dynamics (MD) and (ii) the OPLS-AA force field [6] but with a self-developed charge assignation, similarly to previous works [7], and the re-parametrization of the most relevant dihedrals.

Our preliminary results suggest that peptides with chains up to 3 residues of the simple glycine present a continuous polar domain characterized by a complex hydrogen bonding network. For these ILs, the greater the peptide, the smaller the number of charged centres in close contact but, at the same time, the greater the number of possible hydrogen bonds. On the other hand, when using phenylalanine, the ChPep present two continuous phases, polar and apolar. The apolar aggregates are surrounded by a shell of Ch charged centres suggesting multiple forces ruling the aggregation of the phenylalanyl residue. Finally, this work sets the pace for unveiling more features of these solvents aiming at publishing knowledge that may ease the explanation of the underlying mechanisms of future applications.

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# P124 Determination of nitrate content in lettuce: conformity assessment

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Compared to a few years ago, there is an increasing variety of products available as well as information about them. The quality of the aliments that consumers generally have access to is of great importance, requiring attention and control. At the laboratory level, analysts need to provide the proper control of those products.

Nitrate is naturally present in plants as they absorb it as a source of nitrogen for their growth. Its content is very variable and can be influenced both by intrinsic factors and by the environment.

Most of the nitrate absorbed by humans comes from vegetables. When ingested, it can be reduced to nitrite and form nitrous compounds with relevant toxic effects. In view of these important aspects for human health, the European Union sets maximum nitrate levels in some foods such as lettuce.

In this work, nitrate content in lettuce is determined using ionic chromatography. The results are used to evaluate the risk of the samples being considered improperly compliant or not compliant with legislation, which states the maximum nitrate value in 3 500 mg $NO_3$/kg of fresh lettuce [1]. For this purpose, uncertainty sources associated with each measurement are considered and currently evaluated.

Innovative and user-friendly sampling uncertainty assessment tools are used, which make the work particularly useful for the community of food producers and also for the quality control laboratories.

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# P125 Flavonoid-based deep eutectic solvents: Mechanosynthesis, chemical, thermodynamic and biological characterization

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Deep eutectic solvents (DES) are homogenous mixtures that enables a deep depression of the melting point of their parent compounds. Flavonoids are a well-known family of natural compounds (secondary metabolites), extracted from plants, fruits and vegetables [1]. Due to their antioxidative, anti-inflammatory, anti-mutagenic, anti-carcinogenic, antifungal, antiviral and antibacterial properties, they are found in the composition of several products, including nutraceuticals and cosmetics. Thus, flavonoids are very promising scaffolds with the potential to revolutionize pharmaceutical applications.

In this work, we demonstrate that mechanochemistry is a valuable methodology for DES synthesis using a planetary ball mill. To validate the mechanochemical synthetic route, flavonoid DES were also compared with those prepared by conventional heating. The full range of available compositions was accessed by solid-liquid equilibrium (SLE) diagrams. The experimental SLE phase diagrams were measured using visual turbidimetry and DSC, and the results were compared with the ideal phase diagrams. Toxicity data was also determined.

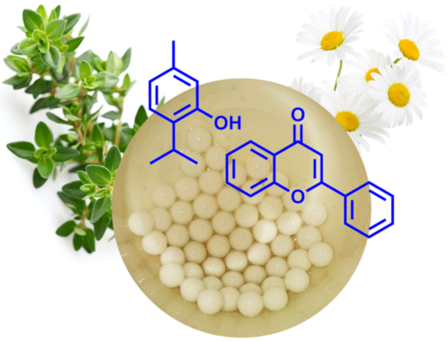

**Figure 1**. Mechanosynthesis of flavonoid-based deep eutectic solvents.

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**References**: [1] A. N. Panche, A. D. Diwan, S. R. Chandra; *Journal of Nutritional Science* **2016**, vol 5.

# P126 Evaluation of the performance of electronically conductive polymer films in the reduction of potentially polluting metal ions

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Chromium is a metal that has oxidation states between -2 and +6, being frequently found in the +3 and +6 states. $Cr^{III}$ is essentially insoluble and poorly absorbed by cellular tissues. $Cr^{VI}$ is easily absorbed by biological membranes, is extremely toxic and even carcinogenic. The main sources of $Cr^{VI}$ contamination in the environment are industrial effluents, which led the European Union to establish an emission limit value for effluent discharges (ELV of 0.1 mg/L $Cr^{VI}$) [1,2]. One of the efficient methodologies in the removal of this ion involves the use of electronically conductive polymers (ECP). These are a class of materials that can combine different properties such as electrical conductivity, physical and chemical stability, electrochromic properties, etc. ECP that have nitrogen atoms in their structure can spontaneously reduce metal ions with high reduction potential through their immersion in the solution containing these ions (e.g. $Cr^{VI}$) being this process called “electroless precipitation” [3].

Polyaniline films were synthesized potentiodynamically on carbon electrodes in aqueous medium from sulfuric monomer solutions at different sweep rates and for different growth loads. The synthesized polymers were characterized voltammetrically in monomer-free solutions – Figure 1. The modified electrodes were exposed to dilute acid solutions of $K_2Cr_2O_7$, by simple immersion, for different periods of time [3].

The evaluation of the effectiveness of the reduction of metallic ions is carried out using analytical methodologies such as UV-Vis spectroscopy [2].

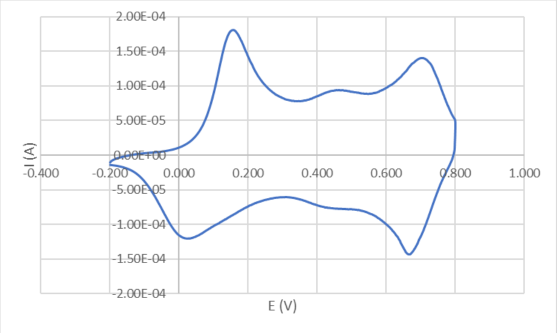

**Figure 1**. Polyaniline voltammogram (v = 100 mV/s) in 0.2 M $H_2SO_4$.

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# P127 Protic ionic liquids as lubricant additives for NEMs/MEMs devices

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Protic Ionic Liquids (PILs) are a subclass of ionic liquids that have recently been considered as potentially good lubricants.[1] They are formed by proton transfer from a Brønsted acid to a Brønsted base and possess the capacity of establishing dense hydrogen bonding. They have the advantage of being easily synthesized, with relatively low cost, and reduced toxicity. Besides, they exhibit low viscosity when compared to the conventional aprotic ILs. PILs have been applied to lubricate several metallic contacts but, to the best of our knowledge, they were never tested as lubrication solutions for silicon surfaces. Lubrication of silicon contacts is an emerging field as it is of extreme importance to find efficient lubricants for nano and microlectromechanical devices (NEMs and MEMs), made of silicon, a hard and brittle material. In this work, we report the use of PILs based on S-containing anions as additives to the commonly used base oil PEG 200 and assess the tribological performance, namely friction and wear, using steel and Si spheres against Si surfaces. All the prepared lubricant formulations were characterized in terms of their water content, viscosity and wettability. The most promising PIL, 4-picolinium hydrogen sulfate ([4-picH][$HSO_4$]), showed excellent tribological performance, both in terms of friction and wear reduction comparing to the model lubricant (see **Figure 1**), making it a very good candidate for future applications in MEMs/NEMs.

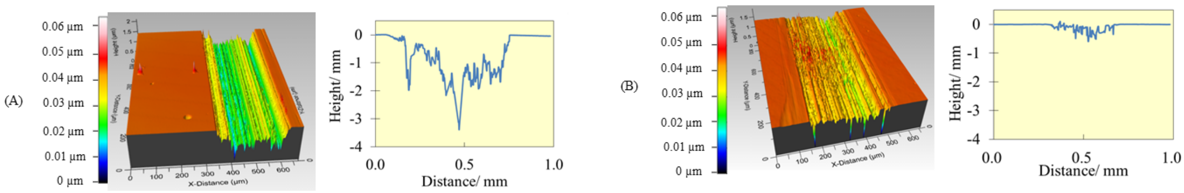

**Figure 1.** Worn Si surfaces after tribological tests using PEG200 (A) and PEG200+[4-picH][$HSO_4$] (B) as lubricants.

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# P128 Tunable electrochemical performance of zinc manganese nanospheres for fit-to-purpose pseudocapacitive devices

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Supercapacitor (SC) systems show a diverse array of desirable features where a large amount of energy needs to be either stored or delivered quickly, features that can be tailored to meet application requirements. Usage of zinc and manganese oxide (ZMO) has been recognized due to its promising and versatile merits both for supercapacitors and lithium-ion batteries. The particular use of ZMO particles for supercapacitor devices has revealed the need of more efficient systems - while its high specific capacitance is typically highlighted, a restricted potential window of activity and rate capability are also identified. Also, the materials preparation methods often rely on complex, multi-step, energy consuming preparation solutions. Thus, it is in the best interest that novel procedures are developed that enable best performance, through simpler, eco-friendlier, and cost worthy solutions for novel electrochemical systems [1–4].

This study focuses on a low energy, one step co-precipitation procedure where commercial zinc and manganese precursors were used. By adjusting the precursor proportion between both metals, the electrochemical response of zinc manganese oxide nanospheres can be tuned. We have unveiled the electrochemical charge storage performance of the system, being able to differentiate the role of zinc but also realized the pseudocapacitive role of manganese. By fine tuning the zinc to manganese ratio, we observed a synergic electrochemical performance, where a wide active potential window of 1.2 V, with high reversibility rate - until 500 mV/s – good specific capacitance (175 F/g at 0.5 A/g), excellent rate capability of 84% and 78% capacitance retention after 5000 cycles, could be achieved. Also, higher specific capacitance could be reached by reducing the zinc to manganese ratio (238 F/g at 0.5 A/g), without significant active potential window loss (1V), and excellent (97%) capacitance retention after 5000 cycles, however, with loss of reversibility at higher scan rates (above 150 mV/s). These results highlight the potential application of this synthetic strategy for ZMO materials for tunable electrochemical energy storage.

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# P129 Natural-based antimicrobial polymeric surfaces for biotechnological applications

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This work involves the development of novel non-toxic polymeric systems, such as coatings, containing bioactive agents able to infer anti-microfouling properties on industrial surfaces, which are in turn applied in various applications such as fluid circuits (e.g., air/water circuits) or in healthcare facilities and devices [1]. The design of these systems will address the incorporation and/or immobilization of promising natural bioactive agents obtained from plant extracts [2] in commercial polymeric formulations. The main work results confirmed high antimicrobial and non-toxic potential of the studied natural extract, expressed by its antibacterial activity against *Staphylococcus aureus MW2* and a cytotoxicity test on liver human cell lines, with a preliminary $IC_{50}$ of 1,01 mg/mL. These results were relevant for the extracts application in polymeric systems, which will be evaluated in terms of their antimicrobial activity and characterized in their mechanical and physical properties to obtain a versatile and ecological material to avoid biocontamination on several surfaces.

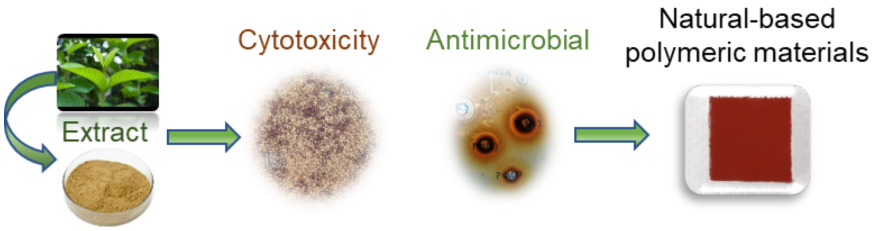

**Figure 1.** Workflow - From a natural extract into antimicrobial surfaces.

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# P130 Novel headspace bar adsorptive microextraction methodology for on-site monitoring of VOCs emitted by the main Portuguese tree species

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Nowadays, climate change persists to increase the incidence of heat waves and periods of drought, which contributes to the development of intense forest fires. The major consequences of extreme wildfires in lives, nature and infrastructures increases the significance of understanding the different sources of sudden changes in the fire's behavior. Studies have suggested that volatile organic compounds (VOCs) emitted from trees can accumulate under vegetation and, in certain atmospheric conditions might be more reactive, accelerating the fire growth [1,2]. In the last decades, modern sample preparation techniques such as solid phase microextraction have shown effectiveness for trace analysis of VOCs through headspace (HS) sampling mode. More recently, bar adsorptive microextraction (BAμE), a novel static-based microextraction technique, was proposed for trace analysis of target compounds of different polarity, showing effective results in various applications due to the high selectivity of the different sorbent coatings used (e.g., polymers and activated carbons) [3].

The present work aimed the development, optimization, validation, and application of a HS-BAμE methodology followed by gas chromatography coupled to mass spectrometry (GC-MS) analysis for monitoring VOCs emitted by the leaves of *E. globulus* Labill. and *P. pinaster* Aiton trees from the Sintra range. For five case study VOCs (α-pinene, β-pinene, myrcene, limonene and 1,8-cineole) the analytical approach achieved under optimized experimental conditions limits of detection and quantification of 25 and 83 ng, respectively, while showing remarkable linearity ($r^2 \geq 0.9966$) between 0.1 to 0.5 μg. Furthermore, the on-site application of the HS-BAμE/GC-MS methodology it was possible to detect four VOCs in the air nearby *E. globulus* Labill. (α-pinene, β-pinene, limonene and 1,7-cineole) and one near *P. pinaster* Aiton (α-pinene), in the range comprised between 0.102 ± 0.002 and 0.311 ± 0.008 μg, showing to be a promising alternative for monitoring VOCs on site in a forest environment, given its high simplicity and easy manipulation.

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# P131 Biochars from seaweed: evaluation of conventional and innovative carbonization routes

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Seaweeds have a great potential as a carbonization feedstock to produce biochars [1]. Marine biomass offers several advantages when compared with terrestrial one, since it does not require the use of arable lands, but also presents challenges associated with high water and salts content. The Portuguese shore has a large variety of green, red, and brown seaweeds from which several compounds with interesting biotechnological applications can be extracted. The solid residue remaining after the extraction process corresponds to ca. 99 % of the original weight and maintains its lignocellulosic structure, thus being still a valuable resource. Present work focuses on the valorization of this residual biomass by exploring conventional thermal carbonization in inert atmosphere (TC) and innovative processes: hydrothermal carbonization (HTC) and acid-mediated carbonization (AMC) [2]. Four seaweeds were selected: *Codium* sp. (CSPgreen), *Asparagopsis armata* (AAred), *Gelidium corneum* (GCred), *Saccorhiza polyschides* (SPbrown). Scanning electron microscopy allowed to evaluate the morphology of the seaweed residues and their derived biochars. Moisture and ash content of the solid residues were quantified, and the inorganic composition of the ash was assessed by X-ray diffraction. Biochars were characterized by $N_2$ adsorption at -196 ºC, pH at the point of zero charge ($pH_{PZC}$), and Fourier transform infrared spectroscopy (FTIR). The yield of the process is dependent on the biomass and carbonization route (**Figure 1**), with the TC yielding higher mass compared to the HTC and AMC since, besides the carbonization of the lignocellulosic structure of the seaweed, the last two routes allow to decrease the inorganic content of the biochar. The AMC and HTC originated biochars with acidic surface chemistry ($pH_{PZC}$ 1.6 to 2.2 and from 2.3 to 4.1, respectively), while the TC yield biochars with $pH_{PZC}$ from 8.0 to 10.5.

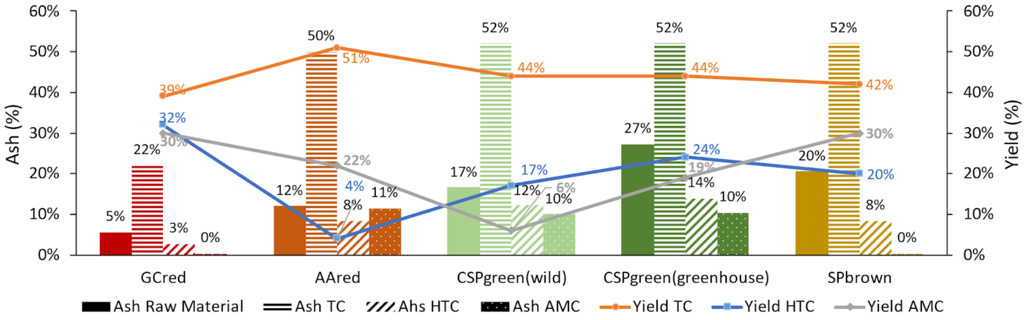

**Figure 1**. Ash content of raw seaweed and derived biochar and carbonization yields.

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# P132 Nanocomposite electrode material - MnCo LDH / N, S doped graphene - synthesized by ball milling process.

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Supercapacitor (SC) are devices applied in electrochemical energy storage (ES) solutions due to diverse operation advantages such as rapid and long-term performance charge-discharge as well as great power density rates [1]. In this sense, researchers have been realizing enormous efforts to performing simple synthesis methods to develop outstanding electrode material for electrode double layer capacitor (EDLC) and pseudocapacitor materials with much more energy-efficient, ecofriendly and smoothly to produce [2]. Among useful composite materials to SC, transition metals (e.g., Mn and Co) and carbon-based material (Graphene - G) have been gaining extensive attention because of elevated specific surface area permitting faster ionic transfer. Additionally, they possess high specific capacitance owing to huge redox active sites, as well cyclic stability and electroconductivity [3]. Moreover, doping G lattice with dual-heteroatoms (pillared agents), namely nitrogen (N) and sulphur (S) avoids yet re-stacking of the graphene 2D layers and improve the energy storage capabilities during electrochemical processes [4]. Herein, in this work, we assess the effect of MnCo layered double hydroxide (LDH) / N, S-G electrode material produced via mechanochemical synthesis, also knowing as ball milling, using N- and S-rich structures, i.e., DMTD ($S_3N_2$) as precursor. They were utilized as active materials proposing new one-step strategy of fabrication of hybrid SC without or free toxic reagents, gram-scalable and reduction of steps. Electrochemical tests (e.g., CV and GCDs) and spectroscopy characterizations displayed interesting behaviors of this nanocomposite for the first in the literature. In 1M KOH electrolyte the MnCo LDH / $S_3N_2$-GF (50:50) electrode composite material attained a motivating specific capacitance, with 107.3 $F.g^{-1}$ at 1 $A.g^{-1}$ and a high coulombic efficiency (ca. 100 %). The study here challenges the assembly of a promising one-route to prepare electrode materials for ES applications.

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# P133 Short-time scale toxicokinetics of inorganic mercury in the saltmarsh plant *Halimione portulacoides*

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Mercury (Hg) is considered a global pollutant due to its ability to spread in the environment, being of great importance to understand its biogeochemical cycle. Wetlands, and particularly saltmarshes, represent the most abundant, fertile, and accessible coastal habitats on Earth, and provide a number of highly relevant ecosystem services, including the regulation of biogeochemical cycles. Saltmarsh plants as *Halimione portulacoides* (*H. portulacoides*) have a key role on Hg biogeochemical cycle, namely by accumulating high levels of this metal in the roots.

The aim of this study was to evaluate the Hg toxicokinetics (uptake, accumulation, elimination) in that saltmarsh plant species comparing between historically exposed and naïve plants. Plants collected in Aveiro Lagoon (Portugal) were exposed to environmentally realistic concentrations of inorganic Hg (iHg) (0.45 µg $L^{-1}$) during 4 h (in hydroponic medium) and under light and dark conditions in order to clarify the influence of light-dependent activity on iHg toxicokinetics. Two sampling sites were chosen with different Hg contamination levels, namely: Laranjo (LAR) as a highly contaminated site, and Chegado (CHE) as a reference site, in order to evaluate the influence of background Hg concentrations on iHg toxicokinetics. Plants were acclimated to the lab for two months before exposure. Leaves, stems and roots samples were collected after 2 h (T2) and 4 h (T4) of exposure to iHg, as well as immediately before exposure (T0) for analysis of total Hg (THg) concentrations.

Total Hg levels in the roots of *H. portulacoides* of both sites were similar at T0, suggesting elimination during the acclimation period and allowing a straightforward comparison of plant responses to the current iHg exposure. At T4, an enhancement of THg levels was recorded in roots of exposed plants from LAR at daylight, while at dark conditions no significant accumulation was found. This data suggest a fast uptake of iHg by the roots of *H. portulacoides* (within a few hours) and that the toxicokinetics of this Hg form depends on the plant activity. An opposite pattern was found for CHE plants at T4 with no significant Hg accumulation at daylight and a notorious enhancement in dark conditions. In general, no significant increases of Hg levels were found in the stems and leaves of plants from both sites over time, indicating a poor translocation of iHg within this short-time scale. Surprisingly, the highest Hg levels were found in plant leaves from both sites and in light and dark conditions, suggesting that the acclimation time was not sufficient to allow plants to eliminate the accumulated Hg through volatilization. Overall, the results highlight the rapid uptake of iHg by *H. portulacoides* roots (within 4 h) and a possible role of the plant activity and Hg historical background on the toxicokinetics of iHg.

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# P134 Microplastics in sediments from inland waters: Bottom-up evaluation of the quantification uncertainty

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The concern with the contamination of the environment with micro(plastics) is very trending nowadays due to the fact that this material is ubiquitous. Actual statistics point that more than 60% of the global composition of marine litter is plastic and about 1.15 to 2.41 million tons of plastic are dumped into oceans every year from rivers [1,2].

The awareness of this threat to the environment and human health attracted the scientific community to the monitoring of microplastics contamination in several aquatic systems and matrices. The monitoring of the level and trends of the contamination by microplastics is essential to determine the relevance and potential sources of this contamination necessary to define strategies to reduce it. The impact of microplastics in rivers and estuarine areas, for instance, is only possible to understand if this contamination is characterized adequately and objectively.

This work presents the first bottom-up evaluation of the uncertainty of microplastics contamination quantification in sediments from north and south Portuguese inland waters. This evaluation involved the identification and quantification of systematic and random effects affecting laboratory analysis. The uncertainty components affecting particles counting were modelled by the Poisson-Lognormal distribution using inputs estimated from duplicate sediment analysis and the analysis of sediments spiked with microparticles. The Monte Carlo Method was used to combine the uncertainty components previously identified. The developed methodology was implemented in a user-friendly MS-Excel spreadsheet used to simulate the probability distribution function of the estimate of the measurand. Distribution percentiles were used to define confidence limits that encloses the true value of the contamination with a defined probability.

Results demonstrated the ubiquitous presence of microplastics in all studied inland waters [3], reaching up to 969 microplastics per kg$^{-1}$ associated with an uncertainty interval of [361; 2932] kg$^{-1}$. After the comparison of the contamination of sediment samples collected in various Portuguese inland waters, it was concluded that several samples had metrologically different contamination for 99% confidence level.

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# P135 Selective production and purification of pentose-rich streams from corncobs

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The use of biomass resources to achieve sustainable economic growth relies on the development of the biorefinery concept. Within this, the biorefinery (bio)chemical platform is considered the best option to produce value-added compounds from biomass. This work aims the development of selective fractionation methods to efficiently recover biomass-derived pentose sugars to be converted into value-added chemicals within the biorefinery framework.Different process options based on mild hydrolysis conditions, namely hydrothermal treatments with liquid hot water (autohydrolysis) and very dilute acid hydrolysis were studied for the selective hydrolysis of hemicellulose fraction of lignocellulosic biomass using corncobs as model feedstock.

The reactions were carried out in a 600 ml high-pressure reactor in a temperature range of 180-220ºC. Hydrothermal treatments enable high solubilization of hemicellulose (up to 94.5%) producing pentose-rich hydrolysates containing up to 31.8 g/l pentoses (74.4% yield), but mainly in the oligomeric form. Depending on the operational conditions, the ratio of oligomeric to monomeric pentoses ranges from 1 to 13, with high severities exhibiting higher proportions of monomeric pentoses.

Dilute acid hydrolysis was also shown to be an efficient method for pentoses production, and the best conditions were found for a sulfuric acid concentration of 25 mM, for which 39.8 g/L monomeric pentoses (36.2 g/L xylose) was obtained. This corresponds to a pentose yield based on the initial (arabino)xylan of 85%. In this case, the ratio of oligomeric to monomeric pentoses is very low (0.03-0.71). The concentrations of sugar degradation by-products were also evaluated and two purification methods for inhibitors removal, including the use of membrane technologies (nanofiltration), activated charcoal adsorption treatment, and selective evaporation/concentration, or combinations thereof were studied.

The data obtained show that due to the low concentration of by-products achieved, the treatments with activated charcoal/concentration of hydrolysates were efficient for inhibitors removal (in particular furans and phenolic compounds) enabling the effective production of high purity pentose streams that surpass 95%, suitable for chemical conversions.

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# P136 $CO_2$ reduction with molybdenum compounds

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$CO_2$ is one of the main greenhouse gases present in the Earth's atmosphere and, currently, there is a huge interest in developing strategies to capture and convert it into chemicals with economical value [1-3]. Among other strategies, $CO_2$ conversion can be carried out electrochemically, using inorganic catalysts inspired on the active site of metalloenzymes [4]. Aiming to design innovative and improved inorganic catalyst for $CO_2$ conversion, in this work, we took inspiration from the active site of formate dehydrogenase (FDH) enzymes (**Fig. 1**) [3,5]. Our strategy was to synthesize new dithiolene groups that mimic the FDH active site pyranopterins (Fig. 1, in red and blue) and the respective molybdenum complexes and to test their ability to convert $CO_2$ into formate and carbon monoxide.

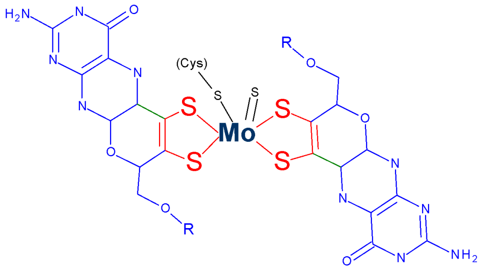

**Figure 1**. Active site structure of a molybdenum-containing FDH [3,5].

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# P137 Ru/USY catalysts for $CO_2$ methanation: effect of precursor type and calcination procedure on particle specific activity

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The conversion of $CO_2$ into methane or synthetic natural gas (SNG) using green hydrogen is one of the most interesting CCU strategies for climate change mitigation. This process, known as $CO_2$ methanation, requires a catalyst to completely reduce $CO_2$ into $CH_4$ (8 $e^-$ gain reaction). In general, a suitable catalytic formulation consists of a supported catalyst with the active sites (typically Ni or Ru) as dispersed as possible over a basic porous metal oxide. Consequently, in last years, catalysts with smaller and, *a priori*, more active metallic particles have been designed by techniques that increase the metal surface/volume ratio and the number of active sites [1]. However, some authors have reported that, in the case of Ru catalysts, low coordinated or monolayer sites induce lower $CO_2$ methanation Turn Over Frequency (TOF) or specific activity than larger nanoclusters, suggesting that there is an optimum Ru particle size and morphology [2].

In order to increase metal dispersion or tune particle size and morphology, various preparation methods have been employed alternative to classic impregnation such as Incipient Wetness Impregnation (IWI) [3], Deposition-Precipitation (DP) [4], and polyol method [5]. On the other hand, it has been reported that the metal precursor could alter the physicochemical properties of the catalyst since it influences the penetration of the solution into the pores as well as the metal-support interaction before calcination. Furthermore, the calcination conditions (temperature and atmosphere) seem to have a great effect on the particle size distribution and morphology [6]. In fact, $RuO_2$ crystals tend to fast grow and agglomerate with increasing temperature under oxidative calcination conditions due to the formation of mobile $RuO_x$ [3].

Accordingly, this work aims to study the effect of synthesis factors such as precursor type and calcination procedure on the particle size and activity of Cs-USY zeolite supported Ru catalysts. First, a series of 3%Ru/USY catalysts are prepared by IWI, varying the Ru precursor salt (ruthenium(III) chloride, acetylacetonate and nytrosil nitrate). After that, a second family of catalysts is prepared through two sequential calcinations, varying the temperature and type of atmosphere (reducing or oxidizing). The results indicate that Ru nitrosyl nitrate ($Ru(NO)(NO)_3$) is the best precursor, since it provides the narrower particle size distribution and higher metal dispersion. Besides, it is concluded that the calcination procedure (temperature and type of atmosphere) has a great influence on particle size and morphology, which determines the specific activity. All catalysts are characterized by XRD, TGA, $N_2$ sorption, $H_2$-TPR and TEM and evaluated for $CO_2$ methanation in a fixed-bed reactor (T = 200-400 °C, P = 5 bar and $H_2/CO_2/N_2$ feed ratio = 36/9/10) in order to relate the physicochemical properties (specially, Ru dispersion) with catalytic performance.

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# P138 Oxidative desulfurization of sulfides with a Mo nanocatalyst

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Producing green fuels is of utmost importance due to increased awareness of the adverse effects of burning sulfur containing fuels on human health and environment. Therefore, removal of such 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 as a promising and highly efficient method owing to its mild operation conditions and high efficiency. Generally, ODS includes mainly two steps: (1) an appropriate oxidizing agent oxidizes the organic sulfur compounds to sulfoxides and sulfones; (2) the oxidation products are removed by suitable methods. Using this approach several researchers are developing cost-effective and environmentally friendly methods for desulfurization, which is still a challenge. In this work a mesostructured material was developed and characterized to be used as 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. The nanomaterial, $NPM_{30}$-Si-inic-Mo, was characterized by infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and by Scanning Electron and Transmission Microscopy (SEM and TEM).

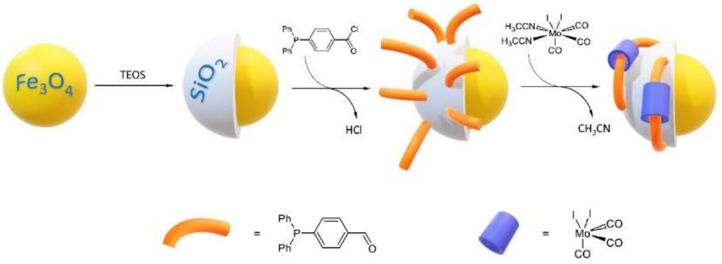

**Figure 1**. Arial 10, aligned center, spacing single.

Then the nanomaterial was tested in the oxidative desulfurization of sulfides to sulfoxides and/or sulfones. 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) and the substrate (diphenyl sulfide and phenyl methyl sulfide). The catalytic tests revealed, in general, promising results. 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. In all reactions it was found that oxidation to sulfoxide and later to sulfone occurred. The most promising catalytic reactions to obtain the sulfone were those that used TBHP as an oxidizer. In the tests carried out with the phenyl methyl sulfide substrate, the yield of 98 and 41% was obtained for sulfone when 1 or 2 mmol of oxidant was used, respectively. For the diphenyl sulfide substrate 34 and 9% yield for sulfone were obtained with 1 or 2 mmol of oxidant, respectively. The yield values obtained for the sulfone with $H_2O_2$ as oxidant are not very promising, needing further studies.

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# P139 On the effects of alkali and alkali-earth metals incorporation into $CO_2$ methanation catalysts formulation

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The environmental concerns regarding the expansion of renewable sources for electricity production are partially related with the characteristic intermittency of these sources. In this way, valorizing the excess of renewable electricity produced during low demand periods through the production of green hydrogen, from water electrolysis, constitutes a promising alternative [1]. Furthermore, $CO_2$ can be successfully converted into synthetic natural gas by using green hydrogen. Overall, this strategy, promising for several industrial sectors, presents important benefits since renewable electricity could be stored in the natural gas grid [1].

$CO_2$ methanation requires the use of catalysts due to the well-known stability of carbon dioxide molecules. In this way, active metals such as Ni, Ru or Rh and supports such as $Al_2O_3$, $SiO_2$, zeolites, hydrotalcites, $ZrO_2$, $CeO_2$, SBA-15 or even MOFs have been widely analyzed in the literature [2]. Among them, the utilization of zeolite-based catalysts has been gaining attention in the last years, mainly due to their easily tunable properties in terms of interaction with water and $CO_2$ or even porosity [2]. Even if promoters such as Ce, Mg or La were identified as interesting over Ni-based zeolites for this reaction, a new approach could arise from the enhancement of $CO_2$ adsorption and activation capacity through the incorporation of alkali and alkali-earth compounds typically present on carbon dioxide capture materials [3].

Thus, in this work bimetallic Ni-based USY zeolite catalysts containing alkali (Li, K and Cs) and alkali-earth (Mg, Ca) metal compounds were prepared using the same conditions (15 wt% of metals; co-impregnation), characterized by $N_2$ sorption, XRD, TGA, $CO_2$ adsorption–desorption, DRS UV-Vis and $H_2$-TPR, and finally tested towards $CO_2$ methanation reaction (86 100 mL $h^{-1}$ $g^{-1}$, $P_{CO2} = 0.16$ bar, $H_2$:$CO_2$ = 4:1) [4].

Based on the results, alkali metals incorporation induced considerably low catalytic performances ($CH_4$ yields below 26%), attributed to their negative impact on the zeolite structure preservation. On the contrary, alkali-earth metal-containing catalysts exhibited lower structural damage. However, the formation of Ni-Mg mixed oxides in Ni-Mg/USY catalyst and $CaCO_3$ during the reaction in Ni-Ca/USY sample could explain their performances, similar or lower than those obtained for Ni/USY reference catalyst. Among the studied metals, calcium was identified as the most interesting ($CH_4$ yield of 65% at 415 °C), which was ascribed to the slight improvement of the $Ni^0$ dispersion [4].

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# P140 $La_2Mo_2O_9$ perovskite nanostructures as catalysts for the oxidative coupling of methane

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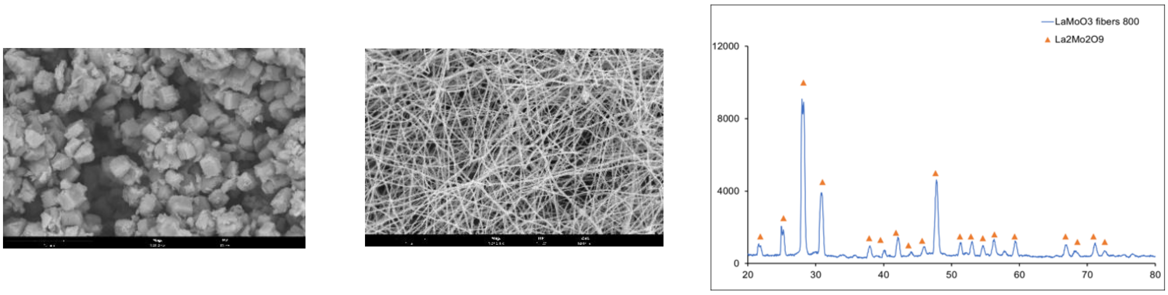
Perovskites ($ABO_3$) are an important class of compounds used as oxygen carriers for redox applications, solid oxide fuel cells, etc. [1,2] Recently, perovskites arise as alternative catalysts for oxidation of hydrocarbons, in particular for the oxidative coupling of methane (OCM) which is attributed to their physical and chemical properties, good thermal and structural stability, high oxygen mobility and low vacancy formation energy [3]. Moreover, perovskites properties possibly will enhance OCM $C_2$ selectivity (ethane and ethylene) and $CH_4$ conversion. [4] Among perovskites, $LaMoO_3$ catalytic and magnetic properties have been investigated and the results obtained strongly depend on their crystal structure and oxidation state of molybdenum. [4]

In this work, $La_2Mo_2O_9$ nanostructured perovskite were obtained with four different shapes (particles, fibers, rods, cubes) using two different experimental approaches, namely: solvothermal method and electrospinning technique that can be easily scale up aiming large-scale synthesis and the production of high-quality crystals at low cost (**Figure 1**). [5] Redox, acid-base properties and crystallite size demonstrated to be dependent of $La_2Mo_2O_9$ morphology. The following crystallite size order was obtained: particles > rods > cubes > fibers. Preliminary results showed that $La_2Mo_2O_9$ nanostructures are active and selective for production of $C_2$ hydrocarbons, being the cubes the most promising ones. Their catalytic activity and selectivity are also influenced by the type of oxidant used ($O_2$, $N_2O$, $CO_2$).



(a) (b) (c)

**Figure 1.** $La_2Mo_2O_9$ perovskite nanostructures: (a) nanocubes; (b) nanofibers and (c) representative X-ray diffraction pattern.

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# P141 Zeolite-based catalysts for biogas dry reforming: Evaluating the influence of the framework type

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As global energy consumption escalates, renewable energy sources are becoming increasingly more necessary towards maintaining and, if possible, reducing $CO_2$ emissions, the main greenhouse gas. Biogas is a promising form of bioenergy whose main components are $CH_4$ and $CO_2$, two major greenhouse gases. Since it can be obtained from the anaerobic digestion of organic materials and, in particular, organic waste, biogas may be a vital steppingstone to achieving a circular and carbon-neutral economy, namely through its conversion into value-added products. Among all, biogas conversion to $H_2$ and CO by dry reforming technology constitutes a promising alternative. However, biogas dry reforming is still an immature industrial process, mainly due to the absence of robust catalysts capable of withstanding the high operating temperatures that cause their deactivation by sintering or/and carbonaceous species formation [1].

Current catalysts for this process may contain noble (e.g., Ru, Rh, Pd, Pt) or transition (e.g., Ni, Co) metals supported over $CeO_2$, $La_2O_3$, $ZrO_2$, MgO, $SiO_2$, $Al_2O_3$, MOFs or zeolites [1-3]. Noble metals are known to resist deactivation, but their high cost and low availability limit their industrial application [2,3]. As such, the cost-effectivity of Ni catalysts motivates further developments on the enhancement of their properties in order to design highly active, selective and stable materials. Several types of nickel-based zeolites have been applied in this reaction due to their easily tuneable properties [1-3]. However, the influence of the type of zeolite framework on catalyst performance requires a systematic study to be properly evaluated and compared.

Therefore, in the present work a series of Ni-based HUSY, HBEA, HMOR, HZSM-5 and HFER zeolites with 15 wt% Ni were synthesized by incipient wetness impregnation and characterized by XRD, $N_2$ sorption, $H_2$-TPR and TEM, and finally tested towards thermal dry reforming of biogas. $CO_2$ and $CH_4$ conversions close to thermodynamics were exhibited by most of the zeolite-based samples, being $H_2$/CO ratios ~1 in all cases. The type of zeolite pores and the $Ni^0$ metallic dispersion, highly influenced by the framework type, presented a significant influence on the achieved performances.

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# P142 Development exploration of synthesis methodologies for the production of sustainable polymers from sugars derived from lignocellulosic biomass

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Studies on the liquefaction of eucalyptus wood residues show that eucalyptus sawdust / sawdust comprises 41% cellulose, 31% hemicellulose, 29% acid-insoluble lignin and 5.1% sugars [1]. However, the fraction composed by sugars has not well been studied and they have not been characterized [2], making it important to study and value these sugars aiming at greater process sustainability, as well as the formation of new molecules from these sugars. In this context, the study of the liquefaction process of lignocellulosic biomass is of great relevance because the chemical reactions that occur during this process, as well as the mechanisms that lead to the formation of sugars, have not yet been properly elucidated, constituting an innovation [1]. Lignocellulosic biomass can become an important raw material for the production of polymers containing sugars. Glucose is the best known breakdown product of cellulose. However, the depolymerization of hemicellulose results in the formation of glucose, as well as other hexoses (mannose, galactose, rhamnose) or pentoses (xylose, arabinose) [3] On the other hand, levulinic acid has been pointed out as a promising molecule with regard to sustainable chemicals, which can be produced from renewable resources such as lignocellulosic biomass [4] The α-angelolactone (AL) can, in turn, be produced from levulinic acid through an intramolecular condensation process followed by dehydration [5], presenting itself as an important raw material for the synthesis of new polymers sustainable [6]. This work has as main objective to investigate the valorization of sugars and their derivatives, present as major components in the aqueous fraction resulting from the liquefaction processes of the wood biomass, aiming at its use in the production of sustainable and biodegradable polymers, which can be applied to processes industrial or agro-industria.

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# P143 Modeling an effective $CeO_2$-supported Ni catalyst for $CO_2$ methanation by DFT: effect of oxygen vacancies and Ni clusters incorporation

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The constant increase in the concentration of $CO_2$, one of the major greenhouse gases, in the atmosphere, is being responsible for the global warming and other climate changes. The identification and mitigation of this chemical has become a global focus to achieve a renewable and environmentally friendly world, demonstrating that an effective measure to decrease the $CO_2$ emissions is to use it as a $C_1$ building block, i.e., the main carbon source to produce value-added chemicals. Among the most important $CO_2$ hydrogenation processes, $CO_2$ methanation has been reported as a promising solution to constrain its emissions and simultaneously reduce energy demands in several fields, such as cement industries, where methane is used in the combustion process [1].

Among the most promising catalysts for $CO_2$ methanation, Ni-based catalysts supported on $CeO_2$ have been shown to improve the reactivity towards $CO_2$ adsorption and activation [2]. Moreover, the interaction of a metal particle with oxide surfaces have been shown to result in major modifications of the electronic structure of the supported species, which will have an impact on the catalytic properties of such systems [3]. In this study, Density functional theory (DFT) calculations have been employed to (1) design the model of $CeO_2$ (111) surface, and study (2) the influence of oxygen vacancies, and (3) the stability and morphology of small $Ni_n$ clusters (n=3, 8, 10 and 13 atoms) incorporated in the slab.

First, an O-terminated $CeO_2$ (111) surface slab is modelled by a 3 x 3 nine-atomic-layer supercell, ensuring a reasonable size to simulate the incorporation of Ni clusters and the reactants adsorption, and that the periodic images do not interact with each other. After that, the influence of having a surface or sub-surface oxygen vacancy is investigated, being the latter more favorable than the former, with an energy difference of 0.73 eV. Besides, the incorporation of $Ni_n$ clusters is evaluated using a genetic algorithm, observing that (i) the exothermic formation of Ni clusters tends to stabilize with increasing cluster size in both gas phase and adsorbed on ceria; and (ii) the presence of a surface oxygen vacancy facilitates the adsorption of these clusters compared to perfect structures or surfaces where the vacancy is in the sublayer and does not have the same influence. Overall, a spherical configuration in surface defected $CeO_2$ is found to be preferrable and specially located on top of surface oxygen, concluding that the strong metal-support interactions derived from the changes in the electronic structure will lead to a more efficient activation or adsorption of $CO_2$.

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# P144 Knoevenagel condensation of benzaldehyde and malononitrile in $scCO_2$ catalyzed by a Zn(II)-CP

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In the scope of the Green Chemistry, the replacement of conventional organic solvents by the so-called "green solvents" (water, biomass derivatives and "advanced" solvents) is a common approach to more sustainable chemical processes. Carbon dioxide, due to its properties, has been successfully regarded as a common replacement when in the supercritical state ($scCO_2$). Moreover, it possesses moderate critical pressure and temperature (p = 73.8 bar; t = 31.1 ˚C) and may be easily separated from the catalytic system by a simple pressure change effect [1].
In the present work [2], the new Zn(II) coordination polymer (CP) $[Zn(L1)(NMeF)]_n \cdot n(NMeF)$ was solvothermally prepared by reacting 5-{(pyren-4-ylmethyl)amino}isophthalic acid ($H_2L1$) with $Zn(NO_3)_2.6H_2O$ in *N*-methylformamide (NMeF). Its potential as catalyst was studied in the Knoevenagel condensation of benzaldehyde and malononitrile in a $scCO_2$ medium.

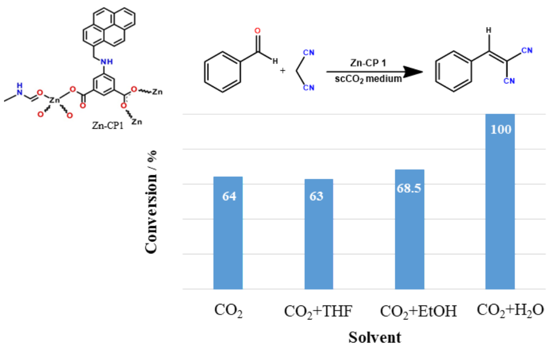

**Figure 1**. Knoevenagel condensation reaction in $scCO_2$ medium using a Zn(II)-CP as catalyst.

An increasing trend was observed in the reaction yield as we moved from THF (aprotic) to EtOH and $H_2O$ (protic) polar co-solvents, reaching the full conversion in the case of water. It was found that $scCO_2$, in the absence of a protic co-solvent, is not the most suitable medium for this reaction. SEM, PXRD, FT-IR and TGA analyses show the high stability of the catalyst throughout the process, which can be recycled without a considerable loss of activity.

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# P145 Oxidative dehydrogenation of ethane over Gallium-Cerium bimetallic oxides

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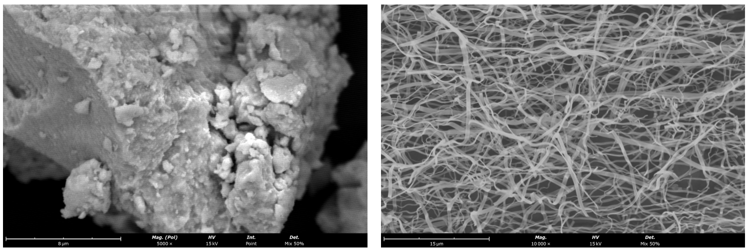
The demand of ethylene has been growing over the decades, reaching >200 million metric tons in 2020 and estimating to reach 300 million metric tons by 2025. [2] Ethylene is a key intermediate to produce other value chemicals such as ethylbenzene, acetaldehyde, acetic acid, styrene, ethanol, among others. [1] Ethylene is produced by several methods, e.g., steam cracking where hydrocarbons and steam are heated to 750–950 ºC. In Europe and Asia, ethylene is obtained mainly from naphtha, gasoil, and condensates. Alternatively, ethylene can be also produced through the direct dehydrogenation of ethane ($C_2H_6 \rightarrow C_2H_4 + H_2$ ; $\Delta H^0_{298} = 137\ \mathrm{kJ/mol}$), which is an endothermic reaction that requires high reaction temperatures between 550-700℃. [3] One main problem is that the reaction under inert atmosphere tends to form coke. Therefore, the dehydrogenation under oxidative atmosphere is an alternative, even though the selectivity may reduce. [4] Recently, other oxidant agents have been studied to replace $O_2$, namely $N_2O$ and $CO_2$. [1] Nakagawa et al. have shown the good efficiency of gallium oxide-based catalysts in the presence of $CO_2$ [5]. Nevertheless, $Ga_2O_3$ deactivates rather quickly but become much more active and stable if together with rare earth oxides. [3] With this in mind, Cerium-Gallium bimetallic oxides (molar ratio Ga/Ce = 0.33, 1 and 3) were synthesized by different methodologies such as electrospinning technique and epoxide addition method, aiming the preparation of catalysts with different morphologies (nanoparticles, fibers) in order to study its shape effect in their catalytic behavior (Figures 1 and 2)). Different oxidants were also tested ($O_2$, $CO_2$, $N_2O$). The catalysts were characterized by different techniques, such as XRD, SEM, TPR and BET.



(a) (b)

**Figure 1**. SEM images obtained after the two types of preparation techniques: a) epoxide addition method, b) electrospinning.

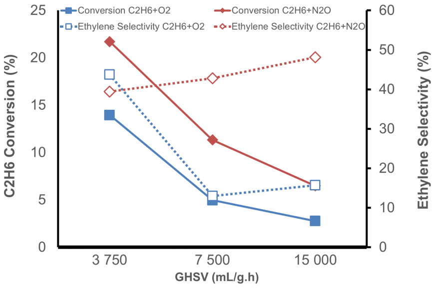


**Figure 2.** Catalytic results of bimetallic Cerium-Gallium oxide (molar ratio = 1) at 600ºC.

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# P146 Electrochemical cyanation of quinolizidine alkaloids

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Quinolizidine alkaloids (QAs) are largely abundant in the Leguminosae family [1], namely in the Lupinus albus L species. [2] Our team developed a process for the preparation of lupanine and sparteine by extraction from Lupinus albus seeds wastewater. [3] These natural products are known for their pharmacological activities, which includes antimicrobial, antihypertensive, as hyperglycemia agents, effects on the central nervous system and uses in asymmetric organic synthesis. [4] Motivated by the potential added value of novel QA derivatives, we explored the selective C-H functionalization of QAs using electrochemistry. [5] Herein we present a new methodology for the cyanation of lupanine using electrochemistry (**Figure 1**).

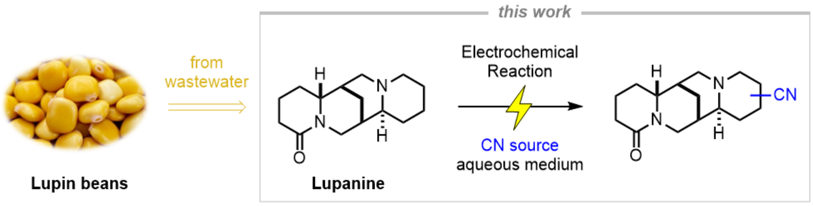

**Figure 1:** Electrochemical cyanation methodology.

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# P147 Synthesis of anticancer drug Busulfan from plastic waste

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The sustainable synthesis of pharmaceuticals is one of the main challenges of the pharmaceutical industry. In this context, plastic waste can be regarded as a potential cheap resource for the production of compounds of interest for the pharmaceutical industry.

Busulfan, 4-methylsulfonyloxybutyl methanesulfonate, is an anticancer drug used to treat chronic myelogenous leukemia and certain blood disorders such as polycythemia vera and myeloid metaplasia, and it has also been applied in some conditioning regimens prior to bone marrow transplant.

In continuation of our work on the depolymerization and valorization of plastic waste,[1-3] in this communication is described the first synthesis of a drug, the anticancer drug Busulfan, from poly(4-hydroxybutyrate) (P4HB) and polybutylene succinate (PBS) waste with moderate overall yields.[4]

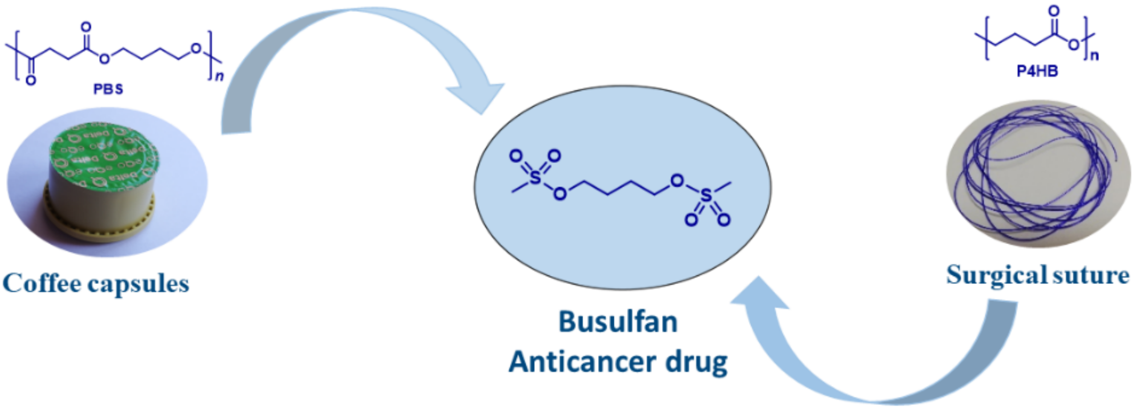

**Figure 1**. Synthesis of the anticancer drug Busulfan from plastic waste.

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# P148 Copper(II) coordination polymers driven by aliphatic dicarboxylate linkers: Self-assembly, structural features and antimicrobial activity

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Coordination polymers (CPs) based on bioactive aliphatic dicarboxylic acids represent a promising class of antimicrobial materials.[1,2] This study highlights the synthesis, characterization and antibacterial activity of two Cu(II) coordination polymers, $\{[Cu(dda)(NH_3)_2]\cdot H_2O\}_n$ (**1**) and $\{[Cu(pim)]\cdot H_2O\}_n$ (**2**). These products were generated by self-assembly from a copper(II) salt, dodecanedioic acid ($HO_2C–C_{10}H_{20}–CO_2H$, $H_2dda$) or pimelic ($HO_2C–C_5H_{10}–CO_2H$, $H_2pim$) acids and aqueous ammonia, followed by characterization by standard methods, including single-crystal and powder X-ray diffraction. Single-crystal X-ray diffraction data show that both crystals are twinned. Compounds **1** and **2** crystallize in the monoclinic system, space group $P2_1/c$, and are composed of copper(II) centers, which are coordinated by the μ-dda$^{2-}$ (**1**) and μ-pim$^{2-}$ (**2**) linkers building 1D or 2D coordination polymer networks, respectively (Figure 1). Antibacterial activity of the obtained products was evaluated against Gram-positive and Gram-negative bacteria, showing a pronounced activity of **1** for *E. coli* and *S. epidermidis*. The obtained results are promising and the research on constructing hybrid polymer materials with **1** and **2** as antimicrobial dopants is currently in progress.[2]

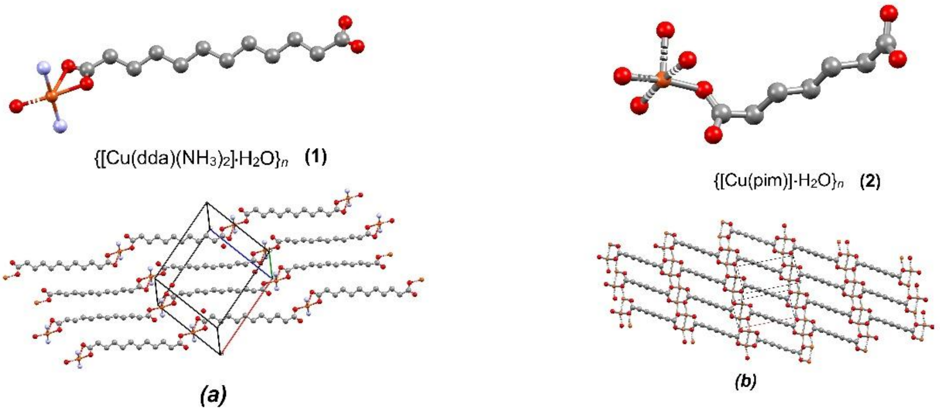

**Figure 1.** Crystal structures and packing patterns of coordination polymers **1** and **2**.

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