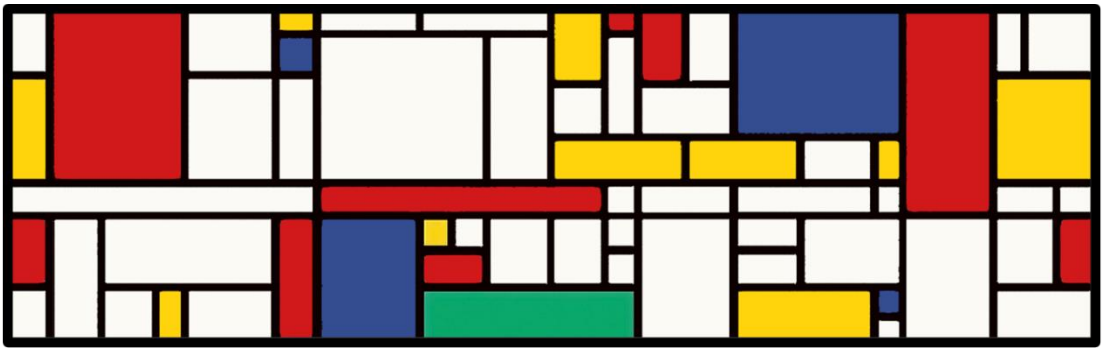

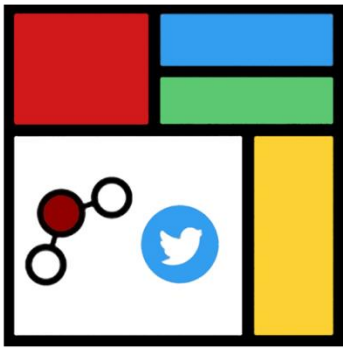

CQE Days 2021
Spring Meeting

27th and 28th of May

ABSTRACT BOOK

KEYNOTE, ORAL & POSTER

CQE
Química Estrutural

CQE Days 2021– Spring Meeting

Centro de Química Estrutural

Book of Abstracts of the CQE Days 2021
27th – 28th May 2021, Lisbon – Portugal

Edited by Ana Paula Carvalho, Ana Cristino, Ana Mourato, Carlos E.S. Bernardes, Gonçalo Justino, Joaquim Marquês, Tânia Morais, Karina Shimizu, and Maria Amália Soares

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List of Participants **130**

Welcome Message

The Centro de Química Estrutural is pleased to organize the 3rd edition of the CQE Days. As you know due to the reality that we are facing since 2020, the 2021 edition will take place live within the virtual platform ZOOM, on May 27th and 28th.

The main purpose of the CQE Days will be to share information about the research work carried out by researchers from CQE, through oral (10 min) and panel communications, aligned with the four Thematic Lines of the 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.

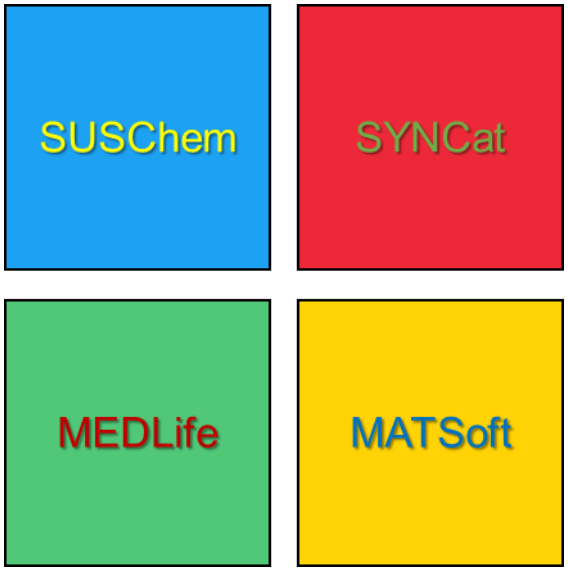
MEDLife - Medicinal and Biological Chemistry for Health, coordinated by Matilde Marques.

In addition to regular communications, the program includes 4 keynotes from well-known invited researchers. The posters will be available on twitter, and a virtual dynamic speed date poster session will provide the opportunity for all participants to present their current results.

Lisbon, May 27th, 2021
The Organizing Committee

CQE Thematic Lines

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



Program

May 27th

09:30 – 10:00	**OPENING SESSION**

Synthesis, Catalysis and Reactivity (SYNCat)

Chairwoman: Luísa Martins

	KEYNOTE
10:00 – 10:40	**K1.** *Powering Metal-Free Catalysts Development for Renewable Energy Processes Through the Rational Bottom-Up Tailoring of C-Networks Surface Properties* **Giuliano Giambastiani** (Institute of Chemistry of OrganoMetallic Compounds, Italy)
10:40 – 11:00	**COFFEE BREAK**
11:00 – 12:30	**O1.** *Rhenium nanoparticles on Norit and graphene as an efficient catalysts for the reduction of aromatic nitro compounds and in the oxidation of 1-phenylethanol.* **Ana P. C. Ribeiro, Beatriz M. Santos, Rute F.C. Faustino, Inês A.S. Matias, Luísa M.D.R.S. Martins, Armando J. L. Pombeiro**
	O2. *Cobalt-based nanofibers for CO2 hydrogenation: effect of f-block elements* **Joana F. Martinho, Joaquim B. Branco, Ana C. Ferreira**
	O3. *Vaporization enthalpies of Grunwald-Winstein binary mixtures at 298 K* **Ruben Elvas-Leitão, Ricardo Nunes, Filomena Martins**
	O4. *Dry reforming of methane over Ni/Zeolites: Structure-reactivity assessment* **Carmen Bacariza, Leila Karam, Nissrine El-Hassan, Pascale Massianic, José M. Lopes, Carlos Henriques**
	O5. *Mn and Fe clusters with O,N-Donor Ligands: Structural characterization and catalytic activity towards oxidative functionalization of cyclohexane* **Nuno Reis Conceição, Oksana V. Nesterova, Dmytro S. Nesterov, M. Fátima C. Guedes da Silva, Armando J. L. Pombeiro**
	LUNCH

Medicinal and Biological Chemistry for Health (MEDLife)

Chairwoman: M. Matilde Marques

	KEYNOTE
14:00 – 14:40	**K2.** *Polypharmacology for neurodegenerative diseases: A Medicinal Chemist's Perspective* **Maria Laura Bolognesi** (Università di Bologna, Italy).
14:40 – 15:00	**COFFEE BREAK**
15:00 – 16:30	**O6.** *Overcoming cisplatin resistance in lung cancer using Ru(II) compounds* **Ricardo G. Teixeira, Ana Isabel Tomaz, M. Helena Garcia, Andreia Valente**
	O7. *Elucidation of potential pathways underlying montelukast neurotoxicity using a metabolomics analysis* **Cátia F. Marques, Gonçalo C. Justino, M. Matilde Marques**
	O8. *New ruthenium-peptide conjugates for selective targeting of breast cancer* **João Franco Machado, Miguel Machuqueiro, Fernanda Marques, M. Helena Garcia, João D. G. Correia, Tânia S. Morais**
	O9. *Anticandidal [CuX(dmp)PPh2R] complexes with aminomethylphosphanes – cell tracking using a phosphane ligand marked with the fluorescent NBD motif* **Radoslaw Starosta, Rodrigo F.M. de Almeida, Jakub Suchodolski, Daria Derkacz, Anna Krasowska**
	O10. *Two-photon activated precision molecular photosensitizer as mitochondria targeting agents* **Ana M. Santiago, Inês F. A. Mariz, Sandra N. Pinto, José M. G. Martinho, Javier Recio, Juan J. Vaquero, Ana M. Cuadro, Ermelinda Maçôas**
16:30 – 17:30	**POSTERS SPEED-DATE**

May 28th

Materials, Soft Matter and NanoChemistry (MATSoft)

Chairpersons: Maria de Fátima Montemor and José Paulo Farinha

	KEYNOTE
10:00 – 10:40	**K3**. *Strategies on catalysts for high performance Lithium-Sulfur Batteries* **Juan Morante** (University of Barcelona)
10:40 – 11:00	**COFFEE BREAK**
11:00 – 12:30	**O11**. *Wavelength selective RCM for large scale characterization of the structural morphology in colloidal photonics* **Laurinda R. P. Areias, Inês Mariz, Ermelinda Maçôas, José Paulo S. Farinha**
	O12. *Electrosynthesis of functional polycatecholamine coatings for biosensing* **Luís C. Almeida, Rui D. Correia, Jorge P. Correia, Ana S. Viana**
	O13. *Development of leucite-based materials reinforced with zirconia for dentistry* **A.C. Branco, T. Santos, M. Polido, R. Colaço, A.P. Serro, C.G. Figueiredo-Pina**
	O14. *The Structure of solutions of active pharmaceutical ingredients: The case study of sulfonamides compounds* **Cátia S. D. Lopes, Catarina V. Esteves, Carlos E. S. Bernardes, Manuel E. Minas da Piedade**
	O15. *Choline Acetate as a potential substitute for Lithium Bromide* **Carla S.G.P. Queirós, Ana F. Cristino, Xavier Paredes, Carlos Nieto de Castro, Fernando J.V. Santos**
	LUNCH

Sustainable Chemistry for the Environment, Energy and Manufacturing (SUSChem)

Chairwoman: Isabel Marrucho

	KEYNOTE
14:00 – 14:40	**K4**. *Biorefining with low cost ionic liquids* **Jason Hallet** (Imperial College London, UK and Lixea OÜ, Bäckhammar, Sweden)
14:40 – 15:00	**COFFEE BREAK**
15:00 –16:30	**O16**. *Sterilization by gamma irradiation of polymeric textiles materials for Personal Protective Equipments* **Diana Silva, Mónica Loureiro, Ana Marques, Rita Rocha, Carla J Silva, Vanessa Machado, João Botelho, João Oliveira, Eduardo Alves, Helena Barroso, Ana P Serro**
	O17. *The role of saltmarsh plants and the effects of seasonal variation in mercury methylation and methylmercury demethylation rates on saltmarsh sediments* **Henrique Zilhão, Rute Cesário, Holger Hintelmann, João Canário**
	O18. *Recovery of Platinum from Leaching Solutions of a Spent Auto-Catalyst through Solvent Extraction by a Thiodiglycolamide Derivative* **Ana Paula Paiva, Ana Méndez, Carlos A. Nogueira**
	O19. *The use of novel Carbon dots based materials for the photocatalytic removal of emergent pollutants* **Gonçalo J.S. Catalão, Olinda C. Monteiro, José V. Prata**
	O20. *Ca-Looping for Thermochemical Energy Storage using waste resources and natural materials* **Eunice Afonso, Paula Teixeira, Carla I.C. Pinheiro**
16:30 – 17:30	**CLOSING SESSION**

Links for the Zoom Sections

May 27th

Morning Sections
Opening & SYNCat Lectures — https://bit.ly/33U2sQ8

Afternoon Sections
MEDLife Lectures — https://bit.ly/3wkVBLP

Posters Speed-Date

MATSoft — **Chairman: João Salvador**
Posters 1 to 24
https://bit.ly/3orLXnM (Pass: 006080)

MEDLife — **Chairwoman: Isabel Correia**
Posters 25 to 45
https://bit.ly/3tSbS97

SUSChem — **Chairwoman: Ana Mestre**
Posters 46 to 69
https://bit.ly/3whLYgS (Pass: 668556)

SYNCat — **Chairwoman: Olinda Monteiro**
Posters 70 to 86
https://bit.ly/3yjaPTg

May 28th

Morning Sections
MATSoft Lectures — https://bit.ly/3olZr4u
Pass: 006080

Afternoon Sections
SUSChem Lectures & Closing — https://bit.ly/3whLYgS
Pass: 668556

Keynotes

K1

Powering metal-free catalysts development for renewable energy processes through the rational bottom-up tailoring of c-networks surface properties

Giuliano GIAMBASTIANI [a,b,*]

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Playing with complex carbon nanostructures and tuning their chemical and electronic surface properties by tailored organic functional groups provides metal-free networks with unique performance in key electrocatalytic processes at the heart of renewable energy technology. The first part of this contribution will be dedicated to a conceptually new approach for the preparation of tailored N-decorated carbon nanotubes (N-CNTs) catalytically active in the electrochemical dioxygen reduction.[1, 3] The rationale of this study lies on the fine-tuning of the adsorption strength of O_2 and/or its reduction intermediates in selected N-heterocycle active sites.

The chemical approach to the exohedral CNTs decoration with N-dopants offers an additional tool for the control of their acid/base surface properties. This aspect is at the core of the second part of this contribution, where the ability and advantages rising from the use of NH-aziridine functionalized CNTs (MW@N_{Az}) as valuable and effective electrocatalysts for the chemoselective CO_2 activation and conversion to CO will be discussed. With a Faradaic efficiency (FE) close to 90% at -1.2 V (*vs*. Ag/AgCl/KCl sat.) and productivity as high as 25 $NL_{CO}h^{-1}g_N^{-1}$, MW@N_{Az} ranks among the metal-free systems with the highest performance reported so far. In addition, the original approach to the catalyst design and synthesis represents a key tool for the comprehension of the mechanism at work for the small molecule activation/conversion [4-6]. Catalyst synthesis, stability and performance in the process will be discussed.

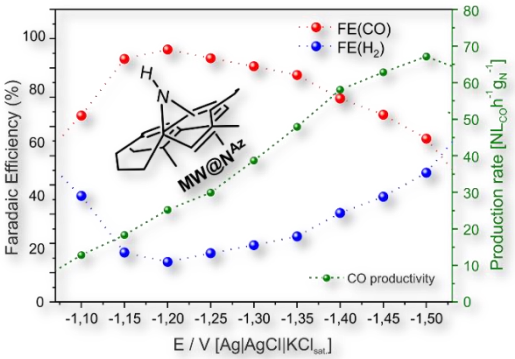

Figure 1. FE and CO productivity of MW@N_{Az} in 0.1M $KHCO_3$.

Acknowledgements

The TRAINER project (Catalysts for Transition to Renewable Energy Future) of the "Make our Planet Great Again" program (Ref. ANR-17-MPGA-0017) and the PRIN 2017 Project Multi-e (20179337R7) "Multielectron transfer for the conversion of small molecules: an enabling technology for the chemical use of renewable energy" are acknowledged for support to this work.

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K2

Polypharmacology for Neurodegenerative Diseases: A Medicinal Chemist's Perspective

Maria Laura Bolognesi *
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Despite robust levels of pipeline activity, neurodegenerative diseases remain one of the most challenging therapeutic areas. The difficulty encountered in developing disease-modifying drugs has been attributed to several factors, including the still incomplete understanding of the causes and the mechanisms by which neurons die, and the consequent paucity of validated targets for therapeutic intervention. Another shared opinion is that drug candidates have failed because they address only one mechanism of the complex pathology underlying neurodegeneration. A possibility to more adequately tackle neurodegenerative disease complexity is the polypharmacology approach. This rests on the design or use of pharmaceutical agents that act on multiple targets or disease pathways. Basically, polypharmacology encompasses two medicinal chemistry modalities: multiple drugs binding to different targets (e.g., drug combinations), and a single drug binding to multiple targets within a given neurodegeneration network (e.g., multi-target-directed ligands). However, several other exist (e.g., codrugs and conjugates), which can be seen as a continuum of polypharmacological opportunities. Each modality has unique features that can be effectively exploited by medicinal chemists. We argue that understanding their advantages and drawbacks helps in choosing the most suitable polypharmacology approach. In this talk, we discuss case studies in Alzheimer disease[2] and multiple sclerosis[3]. In line with an emerging trend, the obtained results suggest that a well concerted polypharmacological approach able to act at multiple, relevant points within the intricate network of neurodegenerative pathways would succeed where other drugs have failed.

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K3

Strategies on catalysts for high performance Lithium-Sulfur Batteries

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The low energy density and relatively high price of traditional lithium-ion batteries (LIBs) are dramatically limiting their application in large-scale energy storage systems, especially in the fast growing field of electric vehicles. To overcome these two limitations, rechargeable lithium sulfur batteries (LSBs) have recently emerged as one of the most exciting alternatives to LIBs owing to their higher theoretical energy density (2600 Wh kg^{-1}, 6 times higher than LIBs of 420 Wh kg^{-1}) and lower cost. However, the practical application of LSBs requires overcoming important challenges.

First, the electrical insulating character of sulfur and lithium sulfides involves a poor utilization of the active material. Besides, the severe volumetric variations (≈80%) during charge/discharge processes lead to the rapid degradation of the electrode integrity. Moreover, the diffusion of soluble lithium polysulfides (LiPS) intermediates into the electrolyte results in poor cycling stability and low Coulombic efficiency. Additionally, the LiPS conversion reaction is generally characterized by slow redox kinetics, limiting the LSBs charge/discharge rate.

In this contribution several strategies will be discussed, developed and applied to improve the electrochemical performance of LSBs based on the rational design and implementation of high-performance LSB cathodes developing materials with excellent electrical conductivity, significant polarity to ensure a strong polysulfide affinity, high catalytic activity toward sulfide redox reactions and with hollow nanostructures to relieve volumetric expansion during charge/discharge. Different options will be revised and their performances discussed.

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Advanced energy materials 11, (2021) 2003507.
Advanced energy materials, (2021) 2100432

K4

Biorefining with low cost ionic liquids

Jason P. Hallett [a,b*]

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[b] Lixea OÜ, Bäckhammar, Sweden
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Ionic liquids (ILs) have proven to be highly tunable 'designer solvents' capable of a wide range of exciting chemistries. However, industrial application at large scale is hampered by high solvent cost. This cost is, however, a tunable feature of the solvent itself – provided the ion selection is handled with a careful eye aimed at limiting synthetic complexity. Lowering the solvent cost will increase the attractive opportunities of ILs for bulk processing of lower cost end products – including such applications as biofuels.

One of the key challenges in biorefining is the initial separation or deconstruction of lignocellulosic feedstock into separate components. ILs offer unique advantages in this area, due to their unusual thermochemical properties. However, there are serious concerns about the economic viability of their use due to the very high cost of most ionic liquids. We have overcome this by redesigning the IL based deconstruction process to use low-cost, acidic ILs for lignin dissolution rather than cellulose dissolution, yielding filterable cellulose and a dissolved lignin for precipitation or conversion to high-value chemicals. We have found that processability of the cellulose is high and lignin recoveries near quantitative.

However, unique challenges arise in the commercialization of a process based on a new solvent. In this presentation, I will discuss the scalability, feedstock expansion, operating conditions and equipment and materials considerations that we have had to overcome in taking this technology to pilot scale. I will also discuss how ionic liquids can be 'tuned' to control cost structure of the final solvent, and what implications this will have for the chemical processes involved. The impact of the solvent on large-scale applications, such as biomass pretreatment, will be discussed, with a focus on performance and process considerations such as how the ILs maintain solvent stability under long-term processing conditions, that they can be recovered and continue to exhibit very good performance after multiple reuses. These properties highlight that the ILs have the flexibility to be useful for a variety of downstream chemical processing techniques, and for use in other applications.

Acknowledgements
I am pleased to acknowledge Fundação para a Ciência e a Tecnologia, reference projects UIDB/00100/2020 and UIDP/00100/2020.

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Oral Presentations

O1

Rhenium nanoparticles on Norit and graphene as an efficient catalysts for the reduction of aromatic nitro compounds and in the oxidation of 1-phenylethanol

Ana P. C. Ribeiro[a,*]; Beatriz M. Santos[a], Rute F.C. Faustino[a], Inês A.S. Matias[a], Luísa M.D.R.S.Martins[a], Armando J. L. Pombeiro[a]

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Rhenium nanoparticles (ReNPs) supported in Norit (activated carbon - AC) and Graphene (G) were prepared through a solvent method using microwave (MW) as the irradiation source. The synthesized heterogeneous catalysts were fully characterized using X-ray powder diffraction, transmission electron microscopy, scattering electron microscopy, Energy-dispersive X-ray spectroscopy, N_2 sorption, Fourier-transform infrared, and ICP (Still to be done). In addition, the catalyst was applied to reduce the aromatic nitro compounds (ANCs) for the first time in aqueous media and using microwave irradiation and the reactions were monitored by following the intensity changes in the UV–vis absorption spectra versus time of reaction. [1] This method proves the advantages of MW by obtaining a high rate constant (*k*), green reaction conditions, simple methodology, easy separation and easy workup procedures in comparison with the traditional method. Moreover, the catalyst can be easily recovered by centrifugation, recycled up to 6 times without any loss of activity. The higher activity of the Re/G catalyst was attributed to higher dispersion and smaller particle size of ReNPs using graphene as support. The ReNPs/G is the catalyst in the solvent free, MW irradiated, oxidation of 1-phenylethanol using hydrogen peroxide shows a significant loss of activity, probably due to the formation of rhenium oxides at the surface of graphene.

Acknowledgements

APCR is thankful to FCT for the Scientific Employment contract IST-ID/119/2018. IASM f is thankful to FCT or her PhD fellowship (SFRH/BD/146426/2019). The CQE reference projects are UIDB/00100/2020 and UIDP/00100/2020.

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O2

Cobalt-based nanofibers for CO_2 hydrogenation: effect of f-block elements

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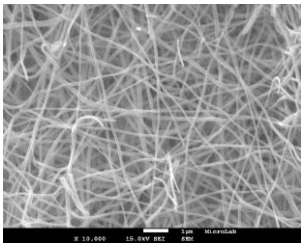
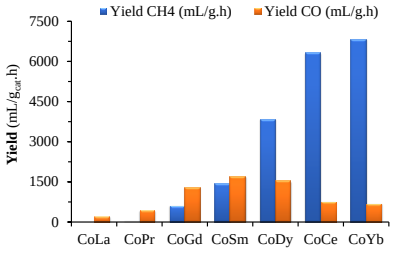
The intensive use of fossil fuels triggered an increase of CO_2 concentration in the atmosphere, being the main contribution to the ´greenhouse effect', the increase of global temperature and climate change. [1] The use of CO_2 as a C1 feedstock in important and viable catalytic processes aiming the production of valuable chemicals and fuels can be a major contribution to avoid such negative effects. [2,3]

The catalytic hydrogenation of CO_2 to methane, the *Sabatier* reaction, associates the reaction of carbon dioxide with hydrogen ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H^0_{298} = -164.9\ \mathrm{kJ/mol}$) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H^0_{298} = -164.9\ \mathrm{kJ/mol}$ usually over supported metals (e.g. noble metals, Ni, Co) at atmospheric pressure. [4] Cobalt-based catalysts exhibit a good performance being very active and selective to methane. However, in order to improve the catalytic behaviour it is essential the addition of promoters, increasing the activity, selectivity and stability. [5]

The purpose of this work was the preparation of cobalt-lanthanide bimetallic oxide nanofibers of the type $5Co_3O_4.3LnCoO_3$ (Ln=La, Pr), $4Co_3O_4.Ln_2O_3$ (Ln=Sm, Gd, Dy, Yb) and $2Co_3O_4.CeO_2$ using the electrospinning technique (Fig.1A) and to evaluate their catalytic performance for the hydrogenation of CO_2. Depending on the lanthanide, the reaction products and its pathway are different: lighter lanthanides (La, Pr, Sm and Gd) produce mainly CO through the reverse water gas shift (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O,\ \Delta H^0_{298} = 41\ \mathrm{kJ/mol}$ $CO_2 + H_2 \rightarrow CO + H_2O,\ \Delta H^0_{298} = 41\ \mathrm{kJ/mol}$), whereas the catalysts with Ce, Dy and Yb are more active and selective to methane (Yield CH_4 > 4000 mL/g_{cat}.h, Fig.1B). Lanthanide intrinsic properties such as ionic radii, reducibility and basicity strongly correlate with the nanofibers' catalytic performance: the lower lanthanide ionic radii and stronger the basicity and oxygen's lability, the higher the catalysts' activity, which suggest a catalytic behaviour mainly governed by the existence of a synergetic interaction between cobalt and lanthanide. Furthermore, stability tests performed over the cobalt-lanthanide bimetallic oxide nanofibers showed their high deactivation resistance, which is an advantage for any catalytic application.



(A)



(B)

Figure 1. (A) SEM image of the cobalt-ytterbium bimetallic oxide nanofibers; (B) Yields to CH_4 and CO over cobalt-lanthanide bimetallic oxide nanofibers (H_2/CO_2=4; GHSV=15000 mL/g.h, T=350 ºC).

Acknowledgements
Authors gratefully acknowledge the support of the Portuguese "Fundação para a Ciência e a Tecnologia", FCT, through the PTDC/EAM-PEC/28374/2017 and UIDB/00100/2020 projects.

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O3

Vaporization enthalpies of grunwald-winstein binary mixtures at 298 k

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Grunwald-Winstein (G-W) binary mixtures, typically ethanol-water, methanol-water, acetone-water, TFE-water and TFE-ethanol in various proportions, have been used for several decades in mechanistic studies where the corresponding G-W model equation,

$$log\ log\ (\frac{k}{k^0}) = mY_X + lN_T + hI + c \quad (1)$$

was applied to the solvolysis of many halogenated substrates [1]. However, if one wishes to compare the performance of this model with other, more complex, models such as the well-known KAT equation,

$$log\ log\ k\ =\ a_0 +\ a_1\alpha +\ a_2\beta + a_3\pi + a_4\delta^2 \quad (2)$$

one cannot do so [2] without the knowledge of the Hildebrand's δ^2 parameter also called the cavity term, which measures the work necessary to create a cavity in a solvent to accommodate a solute/substrate and given by:

$$\delta^2 = \frac{\Delta_{vap}H^0 - RT}{V_m} \quad (3)$$

In the present work we determined, by Calvet microcalorimetry, the vaporization enthalpies of 43 compositions of these mixtures and the corresponding excess enthalpies at 298 K. The results obtained also allow the interpolation of values for any proportion of the mixtures' composition in the range $0 \leq x \leq 1$.

Acknowledgements
The authors acknowledge support from Fundação para a Ciência e a Tecnologia, Portugal (UIDB/00100/2020). This communication is dedicated to the memory of Professor Michael H. Abraham.

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O4

Dry reforming of methane over Ni/Zeolites: Structure-reactivity assessment

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As natural gas is present in remote areas, its transportation is complex and expensive. Therefore, it is converted in place to liquid hydrocarbons through a 2-step process involving syngas production and Fischer-Tropsch synthesis. There are several ways that can be relied on for the synthesis of syngas, but dry reforming of methane (DRM) acquires an additional benefit, which is the consumption of a greenhouse gas (CO_2). However, DRM is still an immature industrial process due to the absence of robust catalysts capable of withstanding the high operating temperature preventing deactivation caused by sintering or/and carbonaceous species formation [1].

DRM catalysts 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]. In this way, 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.

Different types of nickel-based zeolites (e.g., ZSM-5, BEA, MOR, Y, FER, Silicalite-1, ITQ-6) have been applied in this reaction due to their easily tunable properties [1-3]. However, the evaluation of the zeolite framework type and composition effects on the performances requires a systematic study that guarantees proper comparisons.

Consequently, in the present work a systematic series of Ni/Zeolites with different Ni loadings, Si/Al ratios and framework types were synthesized and characterized by ICP, XRD, TGA, N_2 sorption, H_2-TPR, DRS UV-Vis, CO_2 adsorption and TEM in order to assess the influence of these parameters on their physicochemical properties and performances towards DRM. Results evidenced that higher Ni loadings, lower Al contents and the use of USY and MOR zeolites induce higher CO_2 and CH_4 conversions, being H_2/CO ratios ~1 in all cases.

Acknowledgements

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O5

Mn and Fe clusters with O,N-donor ligands: structural characterization and catalytic activity towards oxidative functionalization of cyclohexane

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Following our interest in the study of polynuclear complexes with O,N-donor ligands [1], as potential catalysts in the oxidation and amidation of cyclohexane under mild conditions, novel mixed-valent manganese compounds were synthesized: $[Mn^{II}_2Mn^{III}_2(H^nBuDEA)_2(^nBuDEA)_2(EBA)_4]$ (**1**), $[Mn^{II}_2Mn^{III}_2(H^nBuDEA)_2(^nBuDEA)_2(DMBA)_4]$ (**2**), $[Mn^{II}_4Mn^{III}_2(H^nBuDEA)_2(^nBuDEA)_2(^tBuAA)_8]$ (**3**) and $[Mn^{II}_3Mn^{III}_8O_4(OH)_2(^nBuDEA)_6(DMBA)_8]$ (**4**), through reactions of $MnCl_2$ and/or Mn(0) with *N*-butyldiethanolamine and 2-ethylbutyric (for **1**), 2,2-dimethylbutyric (**2** and **4**) or *tert*-butylacetic (**3**) acids. Another synthesis attempt of **2** resulted most likely in $[Mn^{II}_7Mn^{III}_4O_6(H^nBuDEA)_2(^nBuDEA)_2(DMBA)_8]$ (**5**). The same methodology led to the novel iron(III) compounds: $[Fe^{III}_3O(DMBA)_6(MeOH)_3]Cl{\cdot}MeOH$ (**6**), $[Fe^{III}_3O(DMBA)_6(H_2O)_3]Cl{\cdot}3DMF$ (**7**) and $[Fe^{III}_{22}O_{14}(OH)_4(^nBuDEA)_6(^iBA)_{20}](NO_3)_2{\cdot}10H_2O$ (**8**), *via* reactions of iron(III) chloride or nitrate with $H_2{}^nBuDEA$ (**6** and **8**) or $H_2{}^nBuEA$ (**6** and **7**) and HDMBA (**6** and **7**) or isobutyric acid (**8**).

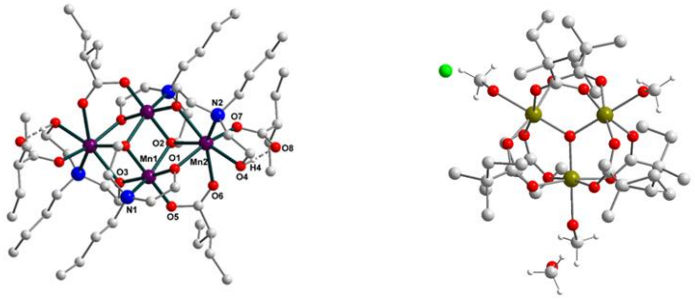

Figure 1. X-Ray crystal structures of $[Mn^{II}_2Mn^{III}_2(H^nBuDEA)_2(^nBuDEA)_2(EBA)_4]$ (**1**) (left) and $[Fe^{III}_3O(DMBA)_6(MeOH)_3]Cl{\cdot}MeOH$ (**6**) (right) [H atoms of carboxylic acid are omitted for clarity].

Compounds **1-3** and **4/5** exhibit catalytic activity towards oxidation of cyclohexane (CyH) for systems having TBHP as oxidant, and the iron complex (**6**) for both H_2O_2 and ^tBuOOH systems (yielding the highest TON of 237). No catalytic activity was reported for systems using *m*CPBA and no oxidative halogenation took place in the studied conditions. Compounds **1** and **8** do not possess catalytic activity regarding amidation of CyH with benzamide using $(^tBuO)_2$ as oxidant.

Moreover, compounds **1-2** and **4** display interesting magnetic properties: single-molecule magnets (SMMs) and antiferromagnetic behavior, respectively [2].

Acknowledgements

This work was supported by *Fundação para a Ciência e Tecnologia* (FCT) (projects UIDB/00100/2020 and UIDP/00100/2020, fellowship SFRH/BPD/99533/2014 and contracts IST-ID/086/2018 and IST-ID/117/2018). NRC acknowledges the *Colégio de Química da Universidade de Lisboa* (grant 15/BGCT/17) and the *Centro de Química Estrutural* (CQE) (grant BL2/2020_IST-ID) for financial support.

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O6

Overcoming cisplatin resistance in lung cancer using Ru(II) compounds

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Multidrug resistance (MDR) plays a key role in chemotherapy failure. Overexpression of membrane transport proteins (such as ATP Binding Cassette (ABC) efflux transporters) that pump drugs out of the cells is one the main mechanisms of MDR that allows for tumor cells survival. A current hot topic in chemotherapy research includes overcoming this limitation by developing inhibitors of these ABC efflux pumps to sensitize cancer cells to drugs.[1] In the recent years, we have been engaged in the development of Ru(II) metallodrugs with transporter pumps inhibitory properties. Our results unveiled two compounds from the "Ru-cyclopentadienyl" family (LCR134 and RT11) with remarkable ability to inhibit P-gp and MRP1 exporters. Both compounds were cytotoxic for breast and ovarian cancer cells, respectively, showing a dual behavior as cytotoxic agents and ABC pump inhibitors.[2,3] Following these studies, other substituents were introduced at the cyclopentadienyl moiety allowing the synthesis of new families of half-sandwich compounds with general formula $[Ru(\eta^5\text{-}C_5H_4R)(bipy)(PPh_3)][CF_3SO_3]$, where R = -CHO or $-CH_2OH$ and bipy = 2,2'-bipyridine functionalized ligands.[4] A total of seven compounds 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, four compounds presented a strong activity against cisplatin-resistant NSCLC cells. Our preliminary results to unveil the mechanism of action of these compounds showed that, when administered at non-cytotoxic doses, some compounds were able to increase cisplatin cytotoxicity in resistant cells up to ~1400-fold by targeting P-gp and MRP-1 transporters and, importantly, they are inducers of collateral sensitivity. As far as we are aware, these are the first ruthenium-based compounds with such a mechanism of action, acting as MDR-selective compounds and taking advantage of the "Achilles' heel" that the overexpression of ABC transporters in cancer cells represents.

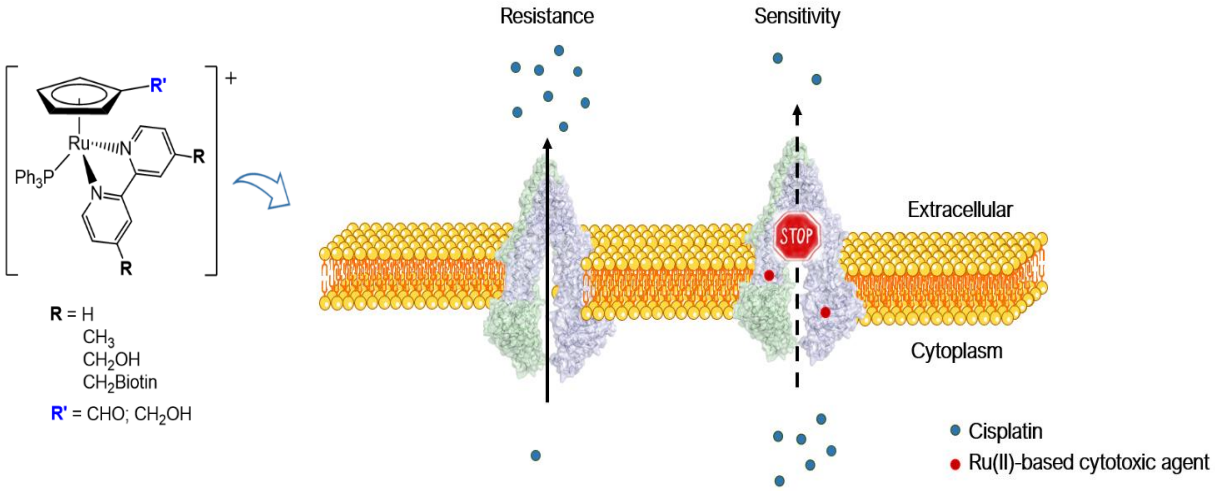

Figure 1. Ru(II)-cyclopentadienyl agents increase cisplatin activity by inhibiting efflux pumps.

Acknowledgements

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O7

Elucidation of potential pathways underlying montelukast neurotoxicity using a metabolomics analysis

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Montelukast (MTK) is widely used for asthma management. This cysteine leukotriene receptor 1 inhibitor is undergoing clinical trials to explore its repurposing for other therapeutic applications, particularly against some neurodegenerative disorders. However, the increasing number of MTK-induced paediatric neuropsychiatric adverse drug reactions requires a proper evaluation of MTK's toxicity to be carried along repurposing studies.

After evaluating the *in vitro* and *in vivo* metabolism of MTK, our goal was to understand the influence of MTK on metabolic pathways using an untargeted metabolomics approach. Test mice were treated with 1.0 mg/kg of MTK by oral gavage once daily for one week and different tissues and fluids were collected for metabolite extraction. An untargeted metabolomics approach was performed by ultra-performance liquid chromatography coupled to high resolution electrospray ionization tandem mass spectrometry, followed by a bioinformatics-driven data treatment approach using XCMS.[1]

Metabolome elucidation and the up/down regulation status of the altered pathways allowed us to elucidate the cellular metabolic processes modified by MTK. Briefly, pathways involved in energy management and in the turnover of biomolecular building blocks (amino acids and nucleosides) were influenced. Regarding the brain tissue, metabolomics data suggest that MTK interferes with neurosteroids and neuromodulators, causing changes in the levels of dopamine, serotonin, and histamine, as well as adenosine and arachidonate. These metabolites play an important role in various brain processes (*e.g.*, signalling and sleep regulation), which may explain the adverse neuropsychiatric effects but also supports the repurposing applications. Decreased glutathione (GSH) levels were also found in MTK-treated animals, consistent with our previous identification of MTK-GSH conjugation. The formation of these conjugates could possibly underlie the downregulation of GSH levels, interfering with the dysregulated neuromodulators by means of a thiolomic-wide change.

Acknowledgements
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O8

New ruthenium-peptide conjugates for selective targeting of breast cancer

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Breast cancer (BC) is one of the most common and lethal types of tumours among women. The fibroblast growth factor receptor (FGFR) is overexpressed in the membrane of breast cancer cells comparatively to the healthy ones in approximately 20% of all the BC cases [1]. This is often associated with multidrug resistance, high metastatic potential, and early cancer recurrence, and thus the overexpression of FGFR constitutes a marker of poor prognosis for the patients with BC. The current treatments clinically available show low efficacy and severe side effects, mostly due to poor tumour selectivity [1]. Therefore, specific therapeutic approaches are urgently needed. Our research group has previously reported the complex $[RuCp(PPh_3)(bipy)][CF_3SO_3]$ (Cp = η^5-C_5H_5, bipy = 2,2'-bipyridine, TM34) that showed promising anticancer activity against several cancer cell lines, including hormone-dependent and triple-negative breast cancer cells [2]. Herein, we aimed to explore the possibility of increasing the selectivity of TM34 towards those cells by tethering it to targeting-peptides that recognize with high affinity and specificity the FGFR receptor, while sparing the healthy tissues (Figure 1). Our molecular dynamics simulations pinpointed the Cp ring of TM34 as one of the most favourable positions for peptide conjugation without affecting its ability to interact with the cell membrane [3]. In this work, we report the synthesis and characterization of a new family of ruthenium-peptide conjugates (RuPCs) bearing the cytotoxic organometallic moiety TM34 conjugated to different targeting peptides with high affinity to the FGFR subtypes 1 to 3. The antiproliferative activity of the RuPCs against human breast cancer cell lines overexpressing the FGFR receptor at different levels will be presented and discussed as well.

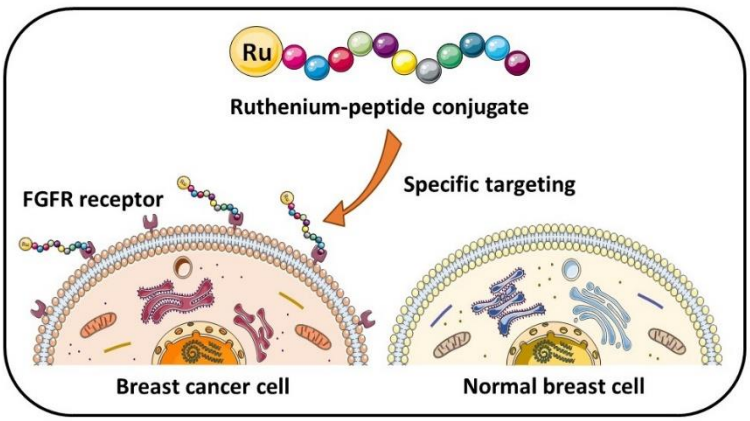

Figure 1. Specific targeting of FGFR(+) breast cancer cells with ruthenium-peptide conjugates.

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Centro de Química Estrutural, Centro de Ciências e Tecnologias Nucleares and Biosystems & Integrative Sciences Institute acknowledges Fundação para a Ciência e a Tecnologia (FCT) for financial support through the Projects UIDB/00100/2020, UID/Multi/04349/2019 and UID/MULTI/04046/2019, respectively. This work was also funded in the scope of the project PTDC/QUI-QIN/0146/2020. J.F. Machado thanks FCT for his doctoral grant (SFRH/BD/135915/2018). T.S. Morais and M. Machuqueiro thank FCT for CEECIND 2017 Initiative for the projects CEECIND/00630/2017 and CEECIND/02300/2017, respectively (acknowledging FCT, as well as POPH and FSE-European Social Fund).

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O9

Anticandidal [CuX(dmp)PPh2R] complexes with aminomethylphosphanes – cell tracking using a phosphane ligand marked with the fluorescent NBD motif

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Recently, as a part of the new ketoconazole derivatives project, we presented two new copper(I) iodide and thiocyanate complexes with 2,9-dimethyl-1,10-phenanthroline (dmp) and diphenylphosphane derivative of ketoconazole (KeP), where ketoconazole acetyl group is replaced by -CH_2PPh_2 unit [1]. Despite not being capable to competitively inhibit the cytochrome P450 14α-demethylase (the azoles' primary molecular target), both complexes proved to be promising antifungal agents towards *Candida albicans*, showing a relatively high efficiency towards the fluconazole resistant strains with - CDR1 and CDR2 or MDR1 efflux pumps overexpression (MIC_{50}s: 0.1–0.78 μM). Additionally, their MLCT based luminescence in aqueous media, allowed to record confocal micrographs which showed that both complexes are situated in spherical structures inside the cells, most likely vacuoles.

To determine the role of the Cu(I) unit and the ketoconazole moiety in the antifungal activity we tested the analogous complexes with PPh_3 and three new diphenylaminometylphosphanes: 1-[(diphenylphosphino)methyl]-4-(4-methoxyphenyl)piperazine, 1-[(diphenylphosphino)methyl]-4-(2-fluorophenyl)piperazine and 7-nitro-4-(4-(diphenyl-phosphinomethyl-piperazin-1-yl)-2,1,3-benzoxadiazole (Ph_2PCH_2-pip-NBD). The results obtained showed that the phosphanes were inactive towards *C. albicans*, but the complexes were only slightly less active than the ones bearing the ketoconazole motif and they are located similarly inside the cells. Most importantly, the complexes showed the same activity towards different mutants.

Particularly useful was the fluorescent Ph_2PCH_2-pip-NBD, which already proved to be an interesting, versatile molecular probe for imaging of living cells (HEK 293T: staining acidic compartments; *C. albicans*: lipid membranes) [2]. Its use allowed to record confocal images in two settings: 488 → 500-600 nm (NBD fluorescence) and 405 → 600-700 nm (MLCT band). The micrographs showed a perfect colocalization of both luminophores in *C. albicans* and NHDF fibroblastic cells.

Summing, the [CuX(dmp)PPh_2R] complexes represent an interesting novel class of anticandidal agents surpassing at least some of the efflux mechanisms. Moreover, the tested compounds do not decompose in the cells and the observed toxicity comes from the molecules introduced to the system.

Acknowledgements

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O10

Two-photon activated precision molecular photosensitizer as mitochondria targeting agents

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Two-photon excitation has become increasingly relevant in biomedical applications for both diagnostic tools and therapeutics. The application of multiphoton fluorescence microscopy for the development of realistic 3D models that mimic biological systems is of high interest among the medical community. In recent years, mitochondria-targeted two-photon fluorophores have emerged as promising anticancer agents. However, the design of photosensitizers combining both mitochondria targeting and two-photon activation is still lagging behind. Here we report new dipolar and quadrupolar quinolizinium and benzimidazolium cations as two-photon activated and mitochondria targeting agents. An efficient light-induced mitochondria damage in living cells is observed upon two-photon excitation in the NIR for some of the dyes. Additionally, interaction with the mitochondria leads to an emission blueshift, most present in the far-red emitting compounds. These observations could lead to the design of new optical tools to interact with the mitochondria and new light responding anticancer drugs.

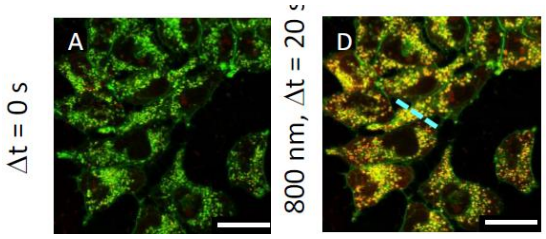

Figure 1. Effect of two-photon irradiation (800 nm, 16 mW, 20 s) on HEK293T cells incubated with ROS probe (MitoSOX) in the presence of Q2 (1.8 μM).

Acknowledgements

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O11

Wavelength selective RCM for large scale characterization of the structural morphology in colloidal photonics

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The development of appropriate methods to correlate structure and optical properties is still a challenge in colloidal photonics. Structural information is mostly obtained by electron, X-ray or optical microscopy methods and X-ray diffraction, while bulk spectroscopic methods and low resolution bright-field microscopy are used for optical characterization.[1] Here we describe the use of reflectance confocal microscopy (RCM) as a simple and intuitive technique to provide a direct correlation between the ordered/disordered structural morphology of colloidal crystals and their corresponding optical properties. We find that wavelength selective RCM provides information on the number, size and orientation of crystalline domains inside supraparticles of colloidal photonic crystals with excellent contrast. The image of the crystalline planes are obtained using a wavelength falling on the stop-band of the structure, while the random scattering from the disordered regions is imaged using a wavelength outside the stop-band.[2]

Our results clearly demonstrate that the full picture given by multi-wavelength RCM can simultaneously and accurately characterize the microstructure and optical properties of spherical colloidal crystals in a fast, non-destructive and easily available methodology.

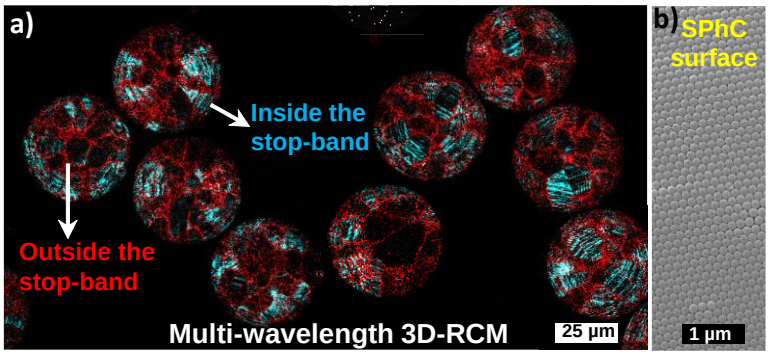

Figure 1: a) Superposition of the RCM images obtained under multi-wavelength illumination, revealing the structural features inside spherical colloidal photonic crystals; **b)** SEM image showing hexagonally packed colloidal nanoparticles at photonic crystal surface.

Acknowledgements
We acknowledge Fundação para a Ciência e a Tecnologia for the funding of CQE projects UIDB/00100/2020 and UIDP/00100/2020. Areias, L. P. R. also acknowledges a doctoral grant from FCT (PD/BD/113533/2015).

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O12

Electrosynthesis of functional polycatecholamine coatings for biosensing

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Bio-inspired polydopamine (PDA) became a reference material in surface modification due to its simple chemical preparation on virtually any solid substrate. The wide range of applications of PDA encompass the biomedical field, biosensors, molecular imprinting, hydrogels, energy storage, among others [1,2], explained by the chemical versatility of its catechol group. The affinity of this chemical group to a variety of surfaces relies on π interactions, hydrogen and coordination bonds. Catechol also displays an important reactivity towards nucleophilic groups, such as amines, thiols or imidazole functionalities, through Michael-type addition or Schiff's base formation. Our recent work demonstrated the suitability of tailored PDA coatings as bioconjugation platforms for affinity [3] and enzymatic [2,4] sensors. PDA is by far the most acquainted catechol-derived coating; however, there are other promising catecholamines, possessing additional chemical groups, whose synthesis and physicochemical properties are not yet satisfactorily explored.

Hereby, a detailed investigation of catecholamines (dopamine, norepinephrine and L-DOPA) and catechol electrosynthesis was carried out, disclosing novel insights of their electropolymerization kinetics and final physicochemical properties of the films. These include: dielectric properties, thickness, chemical composition, porosity and electron transfer properties towards positive and negative redox probes. The gathered results emerge from a combination of surface characterization techniques, specifically, cyclic voltammetry, quartz crystal microbalance, spectroscopy (FTIR, UV-vis, XPS), atomic force microscopy (AFM), ellipsometry and wettability assays. Highly reproducible and quantitatively deposited electroactive films can be achieved for all the monomers, preserving the original pendant groups, which confer pH-dependent electron transfer properties. All polymers display similar adhesion forces towards an amine-modified AFM probe, highlighting the pivotal role of catechol units. This work demonstrates that a controlled electrochemical synthesis of polycatechol, polynorepinephrine and polyDOPA leads to very promising biomimetic materials, alternative to polydopamine, for bioconjugation and electrochemical biosensing applications.

Acknowledgements
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O13

Development of leucite-based materials reinforced with zirconia for dentistry

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Among ceramics, zirconia is one of the most used material to repair/replace damaged/lost dental tissues, due to its high toughness [1]. Glass veneers are usually applied over zirconia frameworks to improve their optical properties [2], but they generally result into chipping [3], leading to extensive wear of the antagonist teeth. Leucite and lithium disilicate are alternative materials to be used without the application of a coating due to their excellent aesthetic properties. However, they present low toughness and therefore fracture and extensive wear of the antagonist teeth and the prosthetic material may occur [4]. Thus, this work aims to develop leucite reinforced with 25 wt% of zirconia nanoparticles in order to improve tribological behavior. The performance of the produced material was compared to that of 100% leucite and 100% zirconia. All samples were produced by unidirectional compressing, followed by sintering at 1000ºC for 6h (75% and 100% Leucite) and 1500 ºC for 2h (zirconia). The samples' mechanical properties were characterized and their tribological behaviour against natural human cusps using a chewing simulator was accessed. The results show that the reinforcement with 25% zirconia reduced the prosthetic materials' wear when compared to 100% Leucite. Regarding wear mechanisms, mild abrasion was observed for the composite (Figure 1B) while for 100% leucite fracture occurred with the spalling of large quantities of material (Figure 1A). In addition, a reduction of dental wear was observed for 75% Leucite when compared to 100% Leucite, being similar to that observed for 100% zirconia. The cusps against 100% Leucite showed abrasion, delamination and fracture (Figure 1C), while the cusps against the composite presented mainly abrasion (Figure 1D).

Overall, the present results are promising, since the wear of the antagonist teeth is much lower than that observed with 100% Leucite, being close to the one obtained with 100% zirconia.

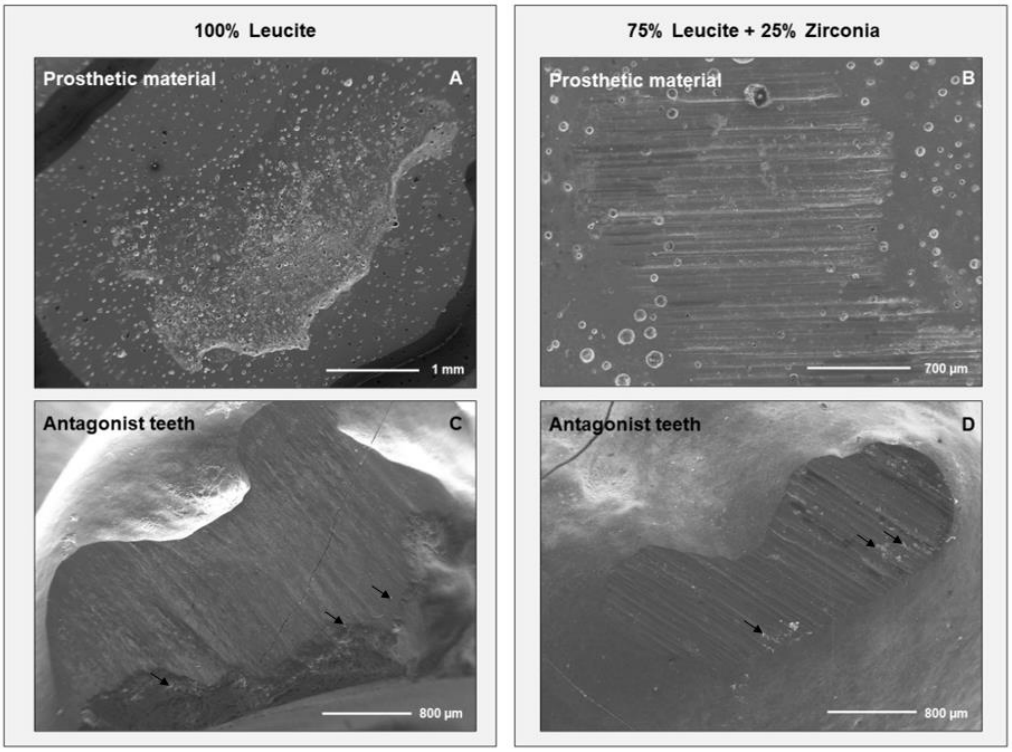

Figure 1. (A) 100% Leucite, (B) 75% Leucite and antagonist teeth pair for (C) 100% Leucite and (D) 75% Leucite. Arrows indicate leucite and dental wear debris.

Acknowledgments

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O14

The structure of solutions of active pharmaceutical ingredients: the case study of sulfonamides compounds

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One of the oldest methods used by man to obtain solid materials is crystallization from solution. However, to this day, limited information exists on how molecules aggregate in a solution to create a crystal, which limits the ability to control this process. As a result, the same molecule often precipitates with different crystal packings, leading to materials with significantly different physical properties (e.g., solubility and bioavailability). This phenomenon known as polymorphism, is critical for the pharmaceutical industry, where the produced materials need to maintain their properties throughout the manufacturing process.[1]

The crystallization control problem can be traced, in part, to the lack of information on the structural transformations occurring in the solution during the nucleation process. Thus, comprehensive knowledge about the molecular aggregation (solution structure) is required if tight control over a crystallization process is in view. In this work, the structure of methanol and acetonitrile solutions of the active pharmaceutical ingredients of the sulfonamide family of compounds (Figure 1) was investigated based on (*i*) the determination of temperature versus concentration phase diagrams, (*ii*) nuclear magnetic resonance studies, and (*iii*) differential scanning calorimetry methods. These studies revealed, so far, that the aggregation of solute molecules begins before saturation of solution is achieved during a cooling crystallization procedure, a finding that contradicts the current nucleation theories. Finally, the crystallization pathway seems to be influenced by the solvent and the solution concentration, suggesting that these factors can be used to control the outcome (crystal phase) of the crystallization process of the sulfonamide compounds.

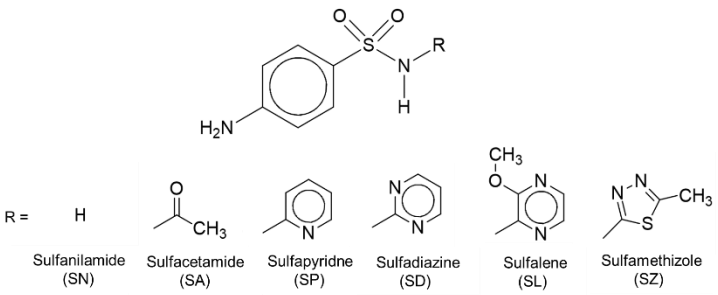

Figure 1. Active pharmaceutical ingredients investigated in this work.

Acknowledgements

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O15

Choline Acetate as a potential substitute for Lithium Bromide

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Ionic liquids have been widely studied due to their unique properties (for example low flammability, negligible vapor pressure, high chemical and thermal stabilities, easy recycling) and potential applicability in a wide range of applications such as heat transport and storage, fuel processing production, pharmaceutical research, and many other fields [1]. The most common ionic liquids (imidazolium and pyridinium based) present high toxicity and nonbiodegradability [2] while choline based ILs can be a less toxic and biodegradable alternative to common ILs [3,4].

Pure choline acetate is solid below 70 ºC, making it difficult to measure some of its thermophysical properties. Only a few studies of its thermophysical properties for very dilute mixtures of choline acetate and water could be found. In this work, new accurate thermophysical properties of the binary system water and choline acetate [Cho][OAc] with an assay ≥ 98%, will be presented and its suitability as a working mixture for absorption refrigeration will be discussed.

Acknowledgements

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O16

Sterilization by gamma irradiation of polymeric textiles materials for Personal Protective Equipments

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Personal protective equipments (PPEs) are essential in preventing/fighting infections, including SARS-CoV-2. Although most of them are disposable, many can be reused, with economic and environmental advantages, if properly sterilized and clean while maintaining the required properties[1,2]. In this work the effect of gamma radiation (GR) on several polymeric textiles intended for PPEs was studied.

Polymeric textiles for PPE (Table 1) were submitted to 20 cycles (C20) of sterilization/washing/drying. First, the samples were sealed in plastic bags and sterilized by GR (25 kGy, 5 kGy/h). The washing process was carried out in a washing/drying machine (HooverAWDPD 4138LH) at 60ºC with 1000 rpm of tumbling and dried at 70ºC (2h30). Wettability, liquid permeability, microstructure, structural properties (FTIR) and mechanical properties were evaluated. The bioburdens of the untreated samples (C0) and the sterility of the C20 samples were studied. Nursing personal at Hospital dos Capuchos and dentists at Clínica Dentária Egas Moniz wore sterilized C0 and C20 samples during an 8h shift. FTIR analysis demonstrated chemical degradation of samples A1 and A2 after 10 cycles (C10). SEM images showed the appearance of holes in the coatings and breaks in the textile fibres, resulting in a significant decrease of the contact angles and of the liquid permeability values. In contrast, A3 maintained the required values for PPE application. The bioburden values were low and statistically similar between samples (10^2 CFU/mL). GR effectively ensured the sterilization of the C20 samples.

In conclusion, depending on the textile/coating composition, GR is a promising sterilization method to reuse polymeric textile materials safely and effectively for PPE application.

Table 1. Coated textiles used in this work.

Sample designation	Textile composition	Membrane/Coating
A1	100% lyocell	Membrane 100% PES, 15 µm thickness
A2	100% polyester	Coating 100% polyvinyl chloride, 340 µm thickness
A3	100% polyester	Membrane 100% polyurethane, 20 µm thickness

Acknowledgements

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O17

The role of saltmarsh plants and the effects of seasonal variation in mercury methylation and methylmercury demethylation rates on saltmarsh sediments

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Saltmarshes are known as accumulation areas for contaminants, namely mercury (Hg) and play an important role in its methylation/demethylation processes. Sampling campaigns were performed in different seasons (spring, summer, etc) in two Portuguese aquatic systems: Tagus Estuary and Ria de Aveiro, both contaminated by anthropogenic mercury.

Non-vegetated and vegetated sediment samples were collected in two saltmarshes from each estuary: Laranjo-LAR and Chegado-CHE from Aveiro, Rosário-ROS and Alcochete-ALC from Tagus. The vegetated samples contained three specific species of plants: *Halimione portulacoides*-HP, *Juncus maritimus*-JM and *Sarcocornia fruticosa*-SF. The experimental design was used to evaluate the influence of plants specie and activity in the methylation of Hg and monomethylmercury (MMHg) demethylation in these environments. For the methylation/demethylation studies, stable isotope tracers of $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^{+}$ were used, followed by isotope-specific detection by inductively coupled plasma mass spectrometry (ICP/MS).

Mercury methylation and MMHg demethylation rates were simultaneously determined in sediments non-vegetated and colonized by halophyte plants. Additional environmental parameters like ambient total Hg (THg) and MMHg concentrations, total content of Iron and manganese, biomass content, organic matter content, etc, were also determined.

Results showed higher concentrations of ambient THg and MMHg in Ria de Aveiro. The highest concentration of THg and MMHg was found in LAR in sediments colonized by JM (58525 ng/g) and in CHE in sediments colonized by HP in summer (334.3 ng/g), respectively. The highest methylation rate was also observed in CHE in sediments colonized by HP in summer (0.452/day) and the highest demethylation rate was found in ROS (25.6/day) during the spring season.

Results suggest that 1) halophyte plants influenced Hg methylation rates, 2) this methylation rates are species-specific and influenced by Hg contamination, and 3) summer conditions enhanced MMHg formation possible due to higher microbial activity during the warmer season coupled with the higher activity of the plant.

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O18

Recovery of platinum from leaching solutions of a spent auto-catalyst through solvent extraction by a thiodiglycolamide derivative

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The well-being of people living in developed countries mostly relies on technological devices that became indispensable, soon put aside and quickly replaced by newer versions. Consequently, the produced huge amounts of end-of-life devices are indeed a real threat to the environment. Spent auto-catalysts (SAC) are wastes containing critical elements such as platinum-group metals (PGMs) [1], and therefore must be regarded as a valuable secondary resource: PGMs are often irreplaceable in their applications, exhibit high prices and show lower contents in natural ores. Accordingly, recycling of PGMs from SACs is a requirement.

Hydrometallurgy is the most environmentally friendly option to recover metals from raw materials [1], and solvent extraction (SX) is often the chosen unit operation to separate the metals of interest in the rich-metal solutions coming from the leaching stage.

In this work, a hydrometallurgical treatment of a SAC containing platinum as PGM was investigated. After optimization of the leaching step, achieved using concentrated HCl solutions and H_2O_2 [2], the aqueous phases were subject to SX with a thiodiglycolamide derivative. The preliminary results obtained with a model solution were promising, but SX for Pt separation from the real SAC aqueous phases did not work as expected. For the adopted experimental conditions, the tested thiodiglycolamide derivative in toluene showed a very good loading performance for both Pt and Fe, but Fe scrubbing and Pt stripping from the organic phases after contact with the SAC solution were not successfully achieved. Hence, the reutilization of the organic solvent needs improvement.

A major part of the research in the hydrometallurgical SX area is carried out with model aqueous phases [3]. This investigation puts in evidence that promising SX systems, working well with lab synthetic solutions, need to be tested with real leaching ones, since the obtained results are often different and much worse.

Acknowledgements
The financial support from Fundação para a Ciência e a Tecnologia, through the CQE reference project UIDB/00100/2020, is gratefully acknowledged.

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O19

The use of novel Carbon dots based materials for the photocatalytic removal of emergent pollutants

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The contamination of the environment by pharmaceutical and personal care products is a major concern needing a solution in the modern world. A possible way to remediate this issue is the removal of these pollutants through photodegradation with the assistance of catalysts.

In this work several environmentally friendly photocatalysts based on carbon dots (Cdots) made from olive mill waste waters and anchored on harmless solid supports (e.g. silica and alumina), were synthesized. After characterization, they were tested in the photodegradation of caffeine, a well-known model pollutant [1]. The photocatalytic samples were made by hydrothermal treatment using olive mill waste waters as carbon dots green precursor, [2] and in the presence of silica or alumina for 4 hours at 250°C, with ethylenediamine used as an additive. For comparative purposes, a different set of samples was prepared by simple mixing Cdots with the supports, in aqueous media.

The samples were characterized from a structural, morphological, and optical point of view and their use as a photocatalyst for caffeine degradation was tested under UV-vis radiation conditions.

The Cdots/SiO_2 sample was the best photocatalyst with the complete caffeine photocatalytic degradation being achieved within 1 hour of irradiation. Considering that photolysis was not able to completely degrade caffeine before the 2 hours of light irradiation, considerable improvements on the degradation of such pollutant were achieved by these catalytic materials. Furthermore, this catalyst was successfully reutilized 4 times without loss of activity. Indeed, it was found that the catalytic performance was even slightly improved in the last cycle which may be due to some possible transformations of the carbon materials, in the catalyst surface, during irradiation.

Acknowledgements
The authors acknowledge to Fundação para a Ciência e a Tecnologia under the projects UIDB/00100/2020, UIDB/00616/2020 and UIDP/00616/2020.

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O20

Ca-Looping for thermochemical energy storage using waste resources and natural materials

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The European Green Deal has the overarching aim of making Europe climate neutral in 2050, and to reach this goal the use of renewable energies is essential. However, the commercial deployment of some renewable energies, such as solar energy at high scale, is still delayed due to the intrinsic supply intermittence and the high costs involved. The development of Thermal Energy Storage systems is important to overcome these issues. Thermochemical energy storage (TCES) was identified as one of the most promising large-scale options using the Ca-Looping (CaL) process [1] based on the cyclic carbonation-calcination reaction of CaO materials (Figure 1).

In this work, four natural Portuguese geological materials/wastes were selected to be used under CaL conditions as TCES materials. Their mixtures with a sludge from a water treatment plant and with silicon carbide (SiC), were also tested for improving the solar absorptivity and stability of the materials. The heat storage density (HSD) of the TCES materials was evaluated during the CaL process in a fixed bed reactor, using a selected gas atmosphere with 50% of CO_2 (in air) and a carbonation - calcination temperature of 800 and 930 °C, respectively. The fresh and used materials were characterized by elemental analysis, N_2 adsorption, SEM, XRD and UV-Vis to determine textural and morphological properties and the mineralogical composition. This study showed that the presence of the sludge in the TCES material hinders the sintering of the CaO particles, which is the main process responsible for the materials deactivation. Additionally, the sludge also impacts the solar absorptance of the sample allowing a higher solar radiation absorptance. Although additive SiC is also an interesting additive material because of its high solar absorptance, the results obtained show that it did not influence the HSD and the stability of the TCES blended material for CaL.

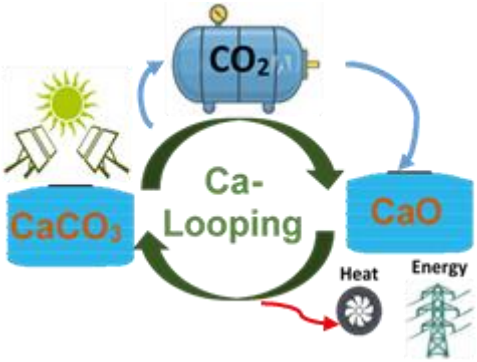

Figure 1. Ca-looping for thermochemical energy storage process

Acknowledgements
Authors thank FCT (UIDB/00100/2020 and UIDP/00100/2020) and Solar-driven Ca-Looping Process for Thermochemical Energy Storage (PTDC/EAM-PEC/32342/2017) for funding.

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Poster Presentations

P1

An Eu(III) complex embedded in a polysulfone host matrix: a flexible film with temperature-responsive ratiometric behaviour

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Temperature is one of the most important parameters since it controls physical, chemical, and biological response of different systems. In nanotechnology and nanomedicine, thermometry is one of the most important parameters and as such it has been intensively explored in the last decade. Several luminescence thermal solutions have been proposed for temperature determination, but trivalent lanthanide-doped materials have unique advantages due to the absence of photobleaching and photoblinking.

Recent studies show that luminescent films are unique when compared with powders or solutions; much easier to manipulate, better flexibility or rigidity and can have predetermined shape or size.

Here we describe the emissive $[C_2mim][Eu(fod)_4]$ (**1**; C_2mim=1-ethyl-3-methyl-imidazolium; fod=1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate), a salt with ratiometric thermal behaviour up to 155°C and the ultrabright and flexible emissive photopolymer film obtained using polysulfone as the host matrix of 10% (w/w) of **1** with temperature-responsive luminescent behaviour.[1]

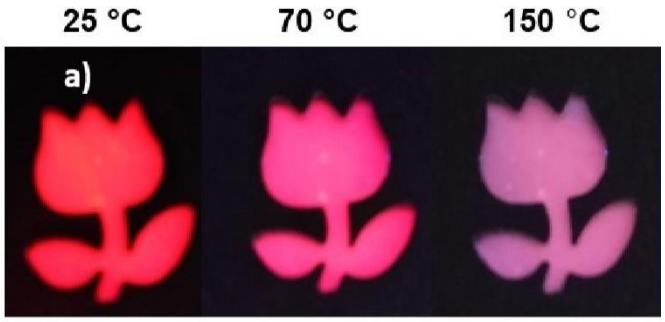

Figure 1. Pictures of 1/PSU under 254 nm lamp at 25, 70 and 150°C

Acknowledgements

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P2

Conservation of decayed stones from cultural heritage: Characterizagrition and potential of new alkoxysilane-based consolidants from NANOCSTONEH project

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Porous stones such as limestone or sandstone were broadly used in buildings, statues, and monuments for many millennia, being still used in many modern constructions. Some of these stones are severely decayed undermining the authenticity and value of cultural heritage where it is embedded.

Alkoxysilane-based materials are an option to face this problem since they are expected to aggregate and bind the outer loosen particles to inner sound stone which avoid the total breakdown of stone surface and slows down the loss rate of the architectural piece.

Among other consolidants, acid and base catalysed alkoxysilane consolidants having tetraethoxysilane (TEOS) and polyethylenoglycol (PEG) as main reagents were developed within the frame of NANOCSTONEH project for this purpose. The applicability of the new consolidants into stone materials was evaluated and the resulting xerogels characterized. The consolidants were mixed with powder, obtained by griding two porous stone varieties, to simulate a real decayed situation and assess its potential to consolidate stones of different mineralogy.

Although quite different xerogel morphologies were obtained, the results showed that both catalytic paths are suitable to prepare consolidants whose application into stone materials is feasible and that can have potential to aggregate loosen powder. Nevertheless, the acid catalysis seems more promising independent on the powder mineralogy, probably due to the higher strength of the typical materials resulting from sol-gel processes driven by acid catalysts.

Finally, the consolidants were applied onto stone materials (limestone and sandstone) and unacceptable and harmful side effects were not observed (e.g. excessive colour alteration or pores occlusion), confirming the potential of these materials as consolidants.

Acknowledgements

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P3

Assessment of the self-healing and inhibition mechanisms in polyolefin-based coating using localized electrochemical and video imaging techniques

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The polyolefin coating and its improved modified formulation were investigated and compared employing localized approach. Localized corrosion behavior was studied in 0.05M NaCl using the combination of Scanning Vibrating Electrode Technique (SVET) and Scanning Ion-selective Electrode Technique (SIET). The obtained distributions of local current density and pH, complemented by the results of video-imaging analysis, SEM and Raman allowed to discriminate the mechanisms of the improved corrosion protection and healing of the coating.

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P4

Surface engineering of bioabsorbable zinc implants with new antibiotic coordination frameworks

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Implantable devices have become a preferred treatment option for the rehabilitation of partially ruptured bone or bone tissues. These are conditions with an increasing incidence in our ageing society, where bone fractures arising from falls are incredibly high. In an era where antibiotic resistance is increasing, bacterial infection as well as the rejection of the implant itself are problems that can imply implant removal or in severe cases, even death.

The success of implanted materials can increase with the use of biocompatible and bioabsorbable implants, such as Zinc (Zn)[1], shown as promising nonpermanent implant, that will degrade while bone recovers over time. Whoever, to overcome the growing trend of implant related infections new strategies are required. The functionalization of Zn surface with an Antibiotic Coordination Framework (ACF) was achieved by electrodeposition.

ACF´s design arose from the need to find more effective drugs to fight infectious diseases, and we have proven that they are a viable pathway to improve the antibacterial activity of already available antibiotics. We have been exploring mechanochemistry as the main synthetic technique in these studies. Nalidixic acid (NALD), a quinolone antibiotic, can coordinate with a variety of metals to form new structures with improved activity[2]. The herein described coordination of nalidixic acid with Ca(II), an important bone component, and the knowledge that infections easily occur during transplantation prompted us to explore the use of such compounds as functional coatings on bone implantable materials.

By using this innovative approach, the physicochemical analysis of the NALD-Ca ACF, prior and after coating Zn, confirmed that the stability of the newly synthesized drug was preserved. The influence of the successful functionalization on Zn degradation and biocompatibility was investigated.

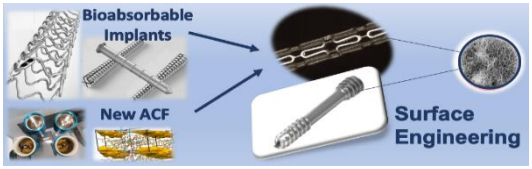

Figure 1. Schematic representation of the synthesis and application of NALD-Ca ACF onto implantable biomaterials

Acknowledgements

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P5

Effect of water on the surface tension of imidazolium based ILs

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Ionic Liquid mixtures (ILs) are studied in view of several applications from chemical synthesis to catalytic reactions or as components in drug delivery systems and complementary participants in drug synthesis, due to their unique characteristics such as negligible vapor pressure, high conductivity and high thermal, chemical and electrochemical stability. The surface tension is a consequence of the unbalanced force field, to which molecules in the interfacial region are subject, having a direct impact on interphase heat and mass transfer processes, with impact on various chemical engineering operations. [1]

In this work the surface tension of binary water + IL liquid mixtures of 1-ethyl-3-methylimidazolium trifluoromethansulfonate ([C_2mim][OTf]) and 1-ethyl-3-methylimidazolium ethyl sulfate ([C_2mim][$EtSO_4$]), between 293-333K, was measured with a K100MK2 tensiometer from Kruss GmbH, based on force measurements, with a precision balance (10 µg resolution) and using a Du Noüy ring. [2] The IL mixtures were prepared by weight and transferred to the sample cell under a dry nitrogen flux, the water content was checked by Karl Fisher method. The surface tension values are the average of more than 20 surface tension values obtained over at least two independent sets of immersion detachment cycles.

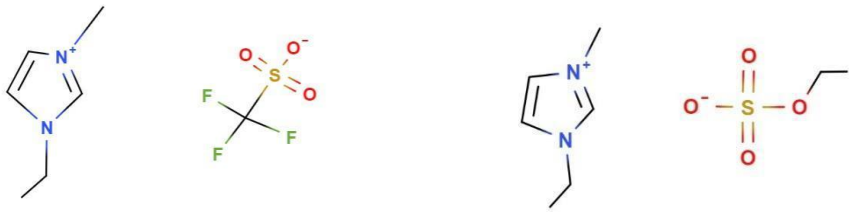

Figure 1. IL [C_2mim][OTf] (left) and [C_2mim][$EtSO_4$] (right)

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P6

Single-Molecule Magnet (SMM) behavior in homoleptic Co(II) complexes of 2-iminopyrrolyl ligands

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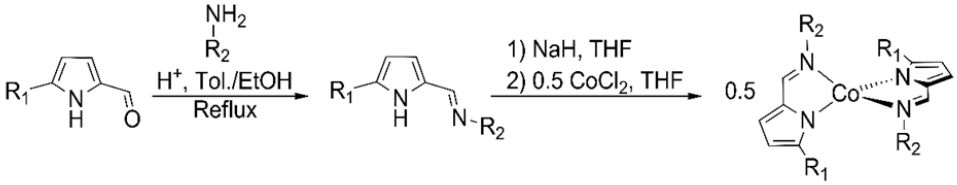
The study of the magnetism of homoleptic Co(II) complexes bearing monoanionic *N,N'*-bidentate 2-iminopirrolyl ligands revealed very interesting properties.[1,2] In fact, the increase of the steric bulk and tuning of electronic properties of the 2-iminopyrrolyl ligands, through the substitution in the position 5 of the pyrrolyl ring with a phenyl group, allowed the detection of SMM behavior in some of the compounds.[2] A family of new four-coordinate complexes of Co(II) were synthesized, showing high values of magnetic anisotropy and energy barrier (*D* and U_{eff}) the majority also displaying SMM behavior under zero dc field (Table 1). A rationalization of the results is attempted in terms of structure-property relationships.

Table 1. Synthesis of new 2-iminopyrrole ligand precursors and their corresponding bis(iminopyrrolyl) Co(II) complexes **1**-**7** and magnetic properties calculated from the ac measurements.



Complex	R_1	R_2	D (cm^{-1})	U_{eff} (K)	τ_0 (ns)
1 [a]	H	2,6-*i*Pr$_2$-C$_6$H$_3$	-69.3	108.90	5.09
2 [b]	C$_6$H$_5$	2,6-*i*Pr$_2$-C$_6$H$_3$	-57.1	130.37	0.60
3 [b]	2,6-Me$_2$-C$_6$H$_3$	2,6-*i*Pr$_2$-C$_6$H$_3$	-48.3	126.62	0.14
4	C$_6$H$_5$	2-*t*Bu-C$_6$H$_4$	-55.3	113.11	1.25
5	3,5-(CF$_3$)$_2$-C$_6$H$_3$	2-*t*Bu-C$_6$H$_4$	-50.5	46.53	223
6	2,6-(MeO)$_2$-C$_6$H$_3$	2-*t*Bu-C$_6$H$_4$	-67.6	81.21	40
7	Ad = 	Ad	-52.6	121.74	0.51

[a] Ref. 1; [b] Ref. 2.

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P7

Evaluation of the surface area and porous volumes of solid materials by different methodologies

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Nitrogen adsorption isotherms at 77 K is the standard method for evaluating specific surface areas (from various models including the BET model) and porous volumes. The method has become increasingly popular with the availability of automatic apparatus. While the automatic determination of the experimental data is obviously advantageous, the correct analysis of the data must still rely on the researcher expertise and critical sense, otherwise misleading results will be obtained. This is the case for the determination of BET surface areas, that depending on the relative pressure range and isotherm shape, can vary significantly. It is the case also for the determination of microporous volumes where the use of the universal "*t*-curve", or the use of a reference isotherm in a non-porous material of composition similar to the material in analysis, can give different results.

The present communication is part of a larger work that involves the study of different "families" of materials. So, in the present case, three activated carbons were selected - nitrogen adsorption isotherms at 77 K in Figure 1 a). For the experimental data in the same sample, differences between BET surface areas reached 14% using different sub-ranges of relative pressure within the range recommended by IUPAC [1]. For the determination of the microporous volumes, the pressure range seems to be more relevant than the type of non-porous reference material.

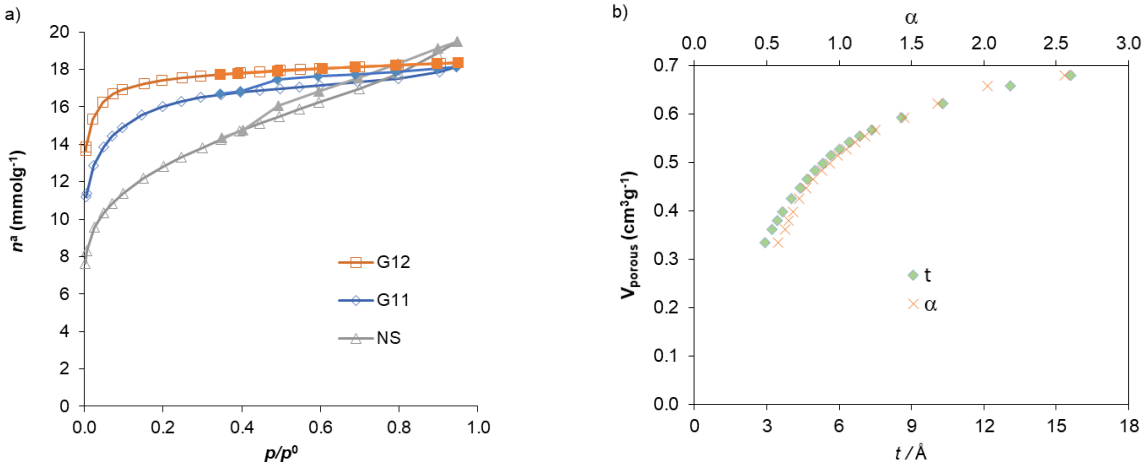

Figure 1. a) N_2 adsorption isotherms at 77 K for the indicated activated carbons (closed points for desorption) and b) comparison plots for the NS sample using the universal curve (*t*) and a reference non-porous carbon (α)

Acknowledgements
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P8

Systematic studies of polymorphism in structurally related compounds: the 4-hydroxybenzoyl family

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Polymorphism, the ability of a molecule to crystallize in multiple solid forms, is commonly observed in many organic compounds. Although the molecule remains the same, packing differences can lead to significant variations in the physicochemical properties (e.g., color, melting point, solubility) of the material. This represents a major concern for various chemical industries (e,g. dyes, agrochemicals, or pharmaceuticals), which rely on the production of materials with highly reproducible properties.

Insights into how the complex interplay of structural, thermodynamic, and kinetic factors influences the formation of different crystal structures at a molecular level, can be obtained by the systematic analysis of polymorphism in families of structurally related molecules. An attractive target for this type of studies is the 4-hydroxybenzoyl family of compounds, with the general formula $HOC_6H_4C(O)R$ (R = H, alkyl), where the molecules differ only in the length of the alkyl chain substituent. These compounds are prone to polymorphic behavior [1-3], displaying examples of both conformational and non-conformational polymorphism, similar and dissimilar polymorphic structures, as well as monotropic and enantiotropic relationships.

This work presents a general overview of our studies on this family of compounds, with a focus on the illustration of how to identify and study different types of polymorphism and show how seemingly small molecular modifications can result in a variety of structural organizations.

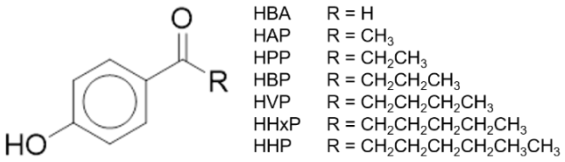

Figure 1. HOC_6H_4COR compounds studied in this work.

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P9

A molecular dynamics force field for fumaric acid derivatives

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Polymorphism, the ability of the molecules of a compound to arrange in different ways in solid-state, is a critical factor in the pharmaceutical industry, due to its ability to influence the physical properties of medicines [1]. Within this scope, molecular dynamics simulations revealed themselves as a powerful tool in the study of this phenomenon, allowing the investigation of many of the characteristics of these materials [2-4]. However, because this theoretical approach is based on parameterized force fields, their validation is required before use, to ensure proper system description. In this work, we describe the development and validation of an OPLS-AA based force field [5] for the study of the fumaric acid family of compounds (used in the treatment of psoriasis), by comparing theoretical predictions of enthalpy of sublimation and single-crystal X-ray diffraction data with experimental values.

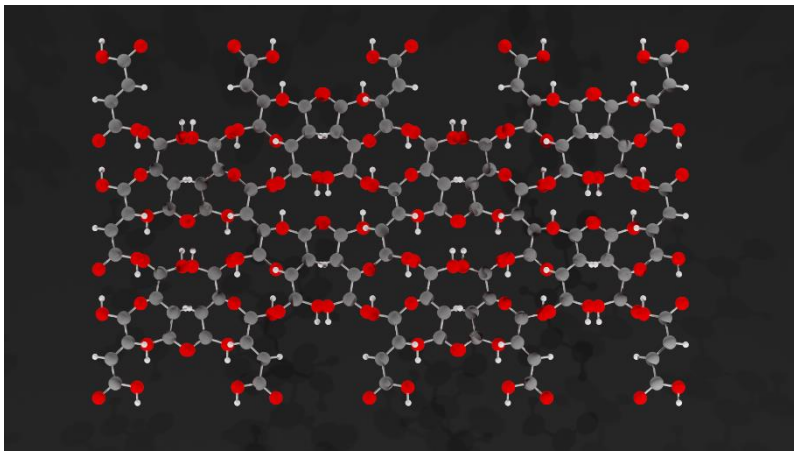

Figure 1. Crystal molecular packing of fumaric acid form I.

Acknowledgements
This work was supported by Fundação para a Ciência e Tecnologia (FCT), Portugal through projects UIDB/00100/2020, UIDP/00100/2020, and PTDC/QUI-OUT/28401/2017 (LISBOA-01-0145-FEDER-028401).

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P10

Fluorescent mesoporous silica nanoparticles for pH sensing

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Fluorescent probes can be used as sensors for measuring pH and detect the presence of other chemical species, and also have many other practical applications, such as corrosion monitoring or biochemical applications like measuring the intracellular pH and monitoring pH-dependent biological processes such as apoptosis or pathogenesis of chronic wounds.[1-4]

Fluorescent sensors used for intracellular pH measurements should have excitation and emission in the visible to near IR range, in order to be detectable by fluorescence microscopy. Their stability over time must be high, and they should not be toxic.

Perylenediimide (PDI) derivatives have been widely used as industrial pigments for tissues and paints, as well as for imaging.[2-4] They show interesting properties, such as excitation in the visible region, high fluorescence quantum yield, high thermal, photochemical and oxidative stability and high electron mobility. PDI derivatives can be synthesized from the commercially available perylene-3,4,9,10-tetracarboxylic acid dianhydride. Substituents can be introduced in the imide nitrogen, affecting the solubility, aggregation or immobilization, or in the bay region, which affects electronic and optical properties.[2-4] Their incorporation in silica nanoparticles should increase their stability and allow the preparation of multiresponsive nanostructures.

In this communication we present the synthesis of new PDI derivatives incorporating groups sensitive to proton concentration in the bay region and alkoxysilane groups in the imide nitrogen to allow their incorporation in silica nanoparticles (SiNPs). We also present the synthesis of such nanoparticles and some of their fluorescence properties.

Acknowledgements

We acknowledge the support of Fundação para a Ciência e a Tecnologia (Portugal) projects UIDB/00100/2020 and UIDP/00100/2020.

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P11

Self-assembled hemimicelles of semifluorinated alkanes: the role of the dipole

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Semi-fluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm) are capable of forming nanostructured Langmuir films at the surface of water or an adequate solid substrate.[1,2] The films are formed by well-defined and mono-dispersed domains, hexagonally packed in organized 2D lattices, which make them very suitable to fabricate self-assembled templates for surface nano-patterning in a bottom-up approach. The tendency to spontaneously form dense, organised surface aggregates is a characteristic of the fluorinated moieties, occurring even at very low surface density.[3]

Recently, we succeeded to model the formation, structure and size of the F8H16 nanodomains using Molecular Dynamics (MD) simulations.[4] In this work, the same methodology was used to study the aggregation of different FnHm molecules in water-supported hemimicelles. The simulation results, which remarkably agree with experimental data, demonstrate that the FnHm arrange in consecutive layers within the hemimicelles. They also display a constant shift (*h*, in Figure 1) along the molecular axis, to align the CH_2-CF_2 dipoles. The internal structure of the hemimicelles and the self-assembling process were rationalised in terms of a geometric model and result from the balance of several factors, most notably the strong electrostatic interactions arising from the dipole of the CH_2-CF_2 bond. We believe our simulation results and quantitative analysis of the interactions are strongly indicative of the driving force for the self-assembling process and explain the pit-centred disc shape of the observed hemimicelles.

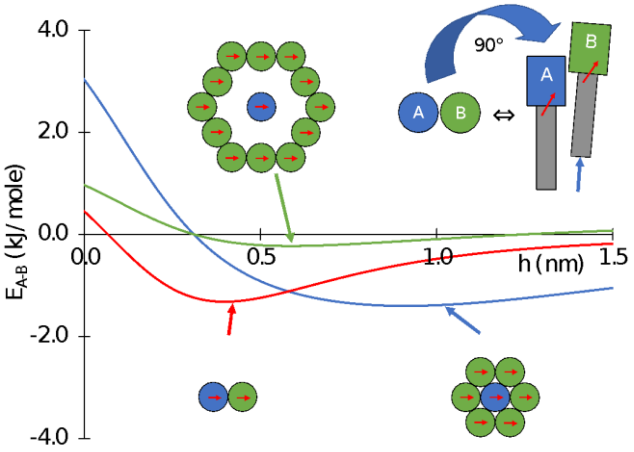

Figure 1. Intensity of the electrostatic interactions among the FnHm molecules as a function of the molecular shift (*h*).

Acknowledgements

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P12

Langmuir films of fluorinated surfactants using molecular dynamics simulations

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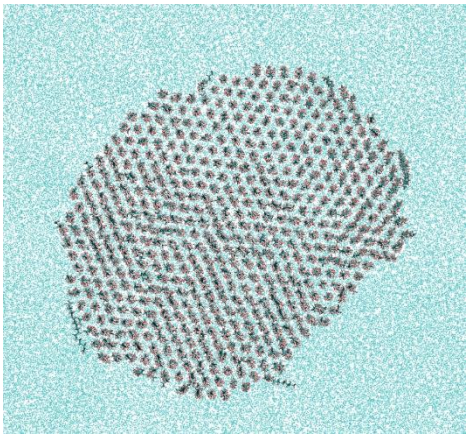
The interfacial properties of fluorinated amphiphiles are well known. Surfaces formed by perfluorinated chains, such as polytetrafluoroethylene or Teflon®, are simultaneously highly hydrophobic and lipophobic. Langmuir films (LB) are useful and well-established model systems. The organization and thermodynamic properties of LB films of hydrogenated fatty acids, alcohols, phospholipids, etc. are well established. On the contrary, studies of Langmuir films of fluorinated amphiphiles have been less systematic and scarcer.

In recent work we have studied Langmuir films of perfluorinated fatty acids and alcohols.[1,2] A combined experimental and computational methodology was used, bringing together experimental data (thermodynamic, atomic force microscopy (AFM), grazing incidence x-ray diffraction (GIXD)) and atomistic molecular dynamics simulations.

In this work, we have focused on long chain perfluorinated substances without a hydrophilic group. These are known to from stable Langmuir films at the surface of water in spite of the lack of amphiphilic character, which is remarkable.[3] Langmuir films of perfluoroeicosane ($C_{20}F_{42}$) have been simulated by atomistic molecular dynamics.

The simulation results are compared with experimental data, in particular GIXD, showing an excellent agreement that fully validates the simulation methodology and interpretations.



MD simulation snapshot (top-view) of an aggregate of $C_{20}F_{42}$ at the air-water interface.

Acknowledgements
Centro de Química Estrutural acknowledges financial support of Fundação para a Ciência e a Tecnologia UIDB/00100/2020.

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P13

VA hydrogels reinforced with aramid nanofibers as cartilage-mimicking materials

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It remains challenging to produce biomimetic materials to be used as substitutes for the cartilage tissue, having the unique combination of properties of high-water retention capacity, mechanical resistance, and low friction. Inspired by the structural similarity of aramid nanofibers (ANFs) to biological fibers [1] such as collagen, we used ANFs to reinforce polyvinyl alcohol (PVA) via hydrogen bonding.

The PVA/ANFs composites were prepared by solution casting method. In brief, PVA was dissolved in dimethyl sulfoxide (DMSO) (15%w/v), water (15%w/v), or trifluoroacetic acid (TFA) (7.5%w/v). ANF solutions (2%w/v), were also prepared in three different solvents: DMSO [2], water, pre-submitting the ANFs to a hydrothermal treatment under acidic conditions [3], and a mixture of TFA:methanesulfonic acid in a ratio of 4:1 v/v. Three different composites (C_D, C_W and C_T) resulted from the combination of PVA:ANF solutions (10:1 w/w), prepared in common solvents. The materials were characterized in terms of swelling, mechanical performance (assessed through uniaxial compressive and tensile tests), and tribological behavior (evaluated by measuring the coefficient of friction (CoF) of the samples against stainless steel balls).

The swelling of hydrogels increased in the following order $C_D<C_W<C_T$. The C_W samples exhibited a superior mechanical resistance under tensile stress when compared to all others, showing higher values of ultimate strength (up to 4.8x) and failure strain (≈1.6x). In response to compression, C_D materials were the most rigid, presenting a modulus of ≈2.6MPa and a maximum strain of ≈36%. Concerning tribological performance, the CoFs of all composites were low and similar (≈0.07) when 5N of force was applied. For 20N, C_W samples had the lowest CoF value (≈0.09).

Our results revealed that the properties of PVA/ANF hydrogels are dependent on the preparation method. The composite prepared in water (C_W) had better mechanical and tribological performance without significantly compromising its swelling capacity.

Acknowledgements

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P14

Sodium alginate/ graphene oxide hydrogels with controlled degradability and suitable mechanical and tribological behaviour for cartilage substitution

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The articular cartilage presents an almost frictionless surface and load-bearing capacity. Hydrogels based on sodium alginate (SA) have been studied as potential cartilage substitution for their resemblance to the extracellular matrix, biocompatibility, and moisture retention properties [1]. Nevertheless, the uncontrollable degradation in saline solutions and the poor mechanical strength of covalent crosslinked SA hinder their application in the tissue engineering field [2]. In this study, graphene oxide was incorporated to develop a material with suitable mechanical and tribological properties for cartilage substitution [3].

A methacrylic modification of the hydroxyl groups of SA's backbone enabled covalent bonding by UV exposure with further ionic bonding of the carboxyl groups with a 1M $CaCl_2$ aqueous solution. The resulting hydrogels presented an equilibrium water content of 85-89%, similar to natural articular cartilage. Hydrogels were characterised regarding their degradation in phosphate buffered saline solution (PBS) for 72h at 37ºC, and the one with the best performance was selected to carry out mechanical and tribological testing. Compressive modulus was evaluated before and after immersion in PBS, falling in the range of values reported in the literature for the articular cartilage and presenting minimal degradation after 72h. The addition of GO in 0.1%, 0.2% and 0.3% (w/v) improved the mechanical properties of the hydrogels, as expected. The mean friction coefficient, μ, was measured in pin-on-disc equipment using pins of porcine knee cartilage as countersurface in either PBS or human synovial fluid lubricating media. It was found that μ decreased as GO content increased. Moreover, smaller μ were obtained in synovial fluid compared with PBS solution.

In summary, a dual step crosslink proved to be a suitable approach to produce SA hydrogels for load-bearing cartilage substitution with tailored degradability and mechanical properties. Furthermore, the presence of GO lowered the μ of composite hydrogels, mimicking the cartilage-on-cartilage contact.

Acknowledgements

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P15

Picolinic acid solubility, aggregation and crystallization studies

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Crystallization is a method to obtain solids from solution that has been around for a long time. However, it remains unclear how molecules aggregate in solution and form a crystal. Many variables can affect the crystallization outcome and the appearance of polymorphs, for instance, the temperature and the solvent used in the crystallization. In order to synthesize only the desired solid, of a given compound, it is crucial to study the existence of polymorphism and what are the exact conditions in which we are able to obtain the pretended crystalline structure [1].

The study of a family of compounds with systematic variations in the molecular structure could help uncover the molecular mechanisms throughout crystallization. Therefore, picolinic acid (Fig. 1), an isomer of nicotinic acid, and the hydroxynicotinic acids, which have been thoroughly studied in our group [2,3], could constitute models for such study. This family of compounds have known biological relevance, namely picolinic acid, is used to chelate several metals, in particular zinc and chromium and these specific chelates are sold as alimentary supplements [4]. In this work some early results on both the solubility (obtained through the gravimetric method) and solid state structure (by means of PXRD) of picolinic acid, at different temperatures, in three polar solvents: water, ethanol (both protic solvents) and acetonitrile (aprotic solvent) will be presented. These results show us that picolinic acid is very soluble in water (for $T \approx 293$ K, $C_{PA} \approx 862.5$ g·kg^{-1}), way less soluble in ethanol ($C_{PA} \approx 57.1$ g·kg^{-1}) and even less in acetonitrile ($C_{PA} \approx 17.0$ g·kg^{-1}). Moreover, its solubility increases with temperature, as expected.

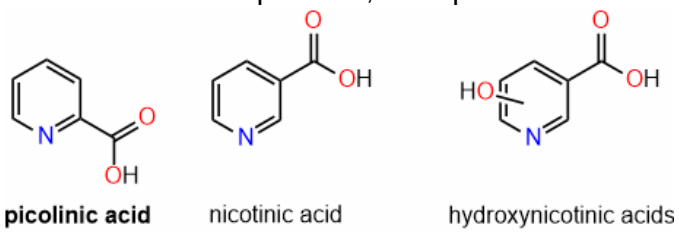

Figure 1. Molecular structures of picolinic, nicotinic and hydroxynicotinic acids.

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P16

Biodegradable metallic implants – how degradation affects bioactivity?

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Zinc (Zn), magnesium (Mg) and their alloys have been proposed as alternative metallic biodegradable materials to support transient wound-healing processes. Once a metallic piece is implanted inside the organism, degradation will occur. The primary reactions occurring upon the insertion of these materials inside an organism are of the utmost importance as the chemical species resulting from the degradation of these resorbable biomaterials will be crucial for the interaction with the surrounding living cells. This, by modulating the composition of the surface layers formed on the devices, will govern the biocompatibility and antimicrobial behaviour of these biomaterials. The biocompatibility will direct the use of these materials, e.g. for bone and/stent applications to favour tissue regeneration, or conversely, when cytotoxic, as local anticancer agents [1-4]. The bioactivity against microbial pathogenic agents will be crucial to aid the increasing antimicrobial resistance to the currently used drugs, particularly if endowed with antibiofilm activity.

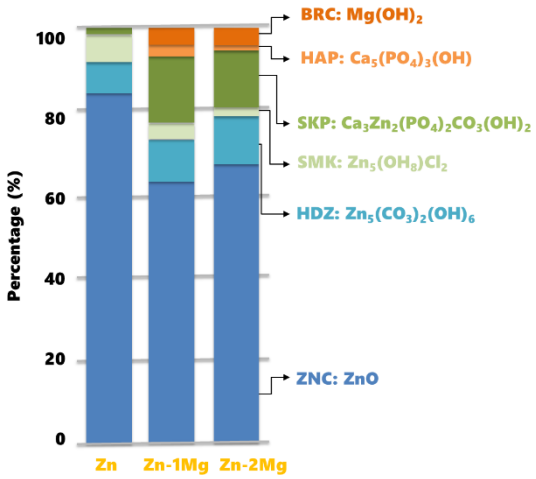

Figure 1. Chemical atomic elements percentage (c) in association with the compounds (d) present on the corroded surfaces of Zn, Zn–1Mg and Zn–2Mg

Acknowledgements
The authors thank to Fundação para a Ciência e a Tecnologia (UIDB/00100/2020).

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P17

Delivery of anti-inflammatory peptides from functionalized hydrogels suitable as therapeutic contact lenses

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Peptides have gained interest as drug candidates for the development of novel and safer medicines [1]. Kyotorphin (L-Tyr-L-Arg) is a small endogenous neuropeptide, which exhibited analgesic activity. To improve its membrane permeability, some derivatives (i.e. KTP-NH_2, Ibuprofen-KTP, Ibuprofen-KTP-NH_2) were previously designed. These derivatives also demonstrated to inhibit the liberation of pro-inflammatory cytokines [1,2]. The development of permeable drugs for topical application, able to provide a therapeutic effect in the back of the eye without need of intraocular injections, is a trending topic in ophthalmology. Herein, a KTP derivative (KTP-NH_2) was selected as a model peptide to investigate the possibility of its loading and release from therapeutic contact lenses (CLs), which could act as drug-reservoirs for the daily sustained release of the peptide.

Two CL materials (i.e. HEMA and HEMA-NVP-TRIS hydrogels) were investigated as potential CL backbone. *Autodock* software was used to model the molecular interactions between the monomers and the peptide. Based on the results, AAc (acrylic acid) and MAA (methacrylic acid) were incorporated in the prepolymer mixture as functional monomers. After polymerization, the peptide was loaded into the hydrogels by soaking for 72h.

HEMA-NVP-TRIS hydrogels released the loaded peptide within the first hour in vitro (Figure 1). HEMA-based hydrogels sustained the release for about 8h. The incorporation of functional monomers increased the amount of drug released over time. The swelling of HEMA-NVP-TRIS lenses (≈ 65%) was higher than for HEMA-based lenses (≈ 45%) due to the high water uptake of NVP [3]. All designed hydrogels showed suitable light transmittance properties for their use as contact lens materials.

The release of KTP-NH_2 for 8h from HEMA-based hydrogels is compatible with their use of daily therapeutic lenses for the treatment of inflammatory ocular conditions. Further investigation is needed to assess the peptide permeation to the back of the eye.

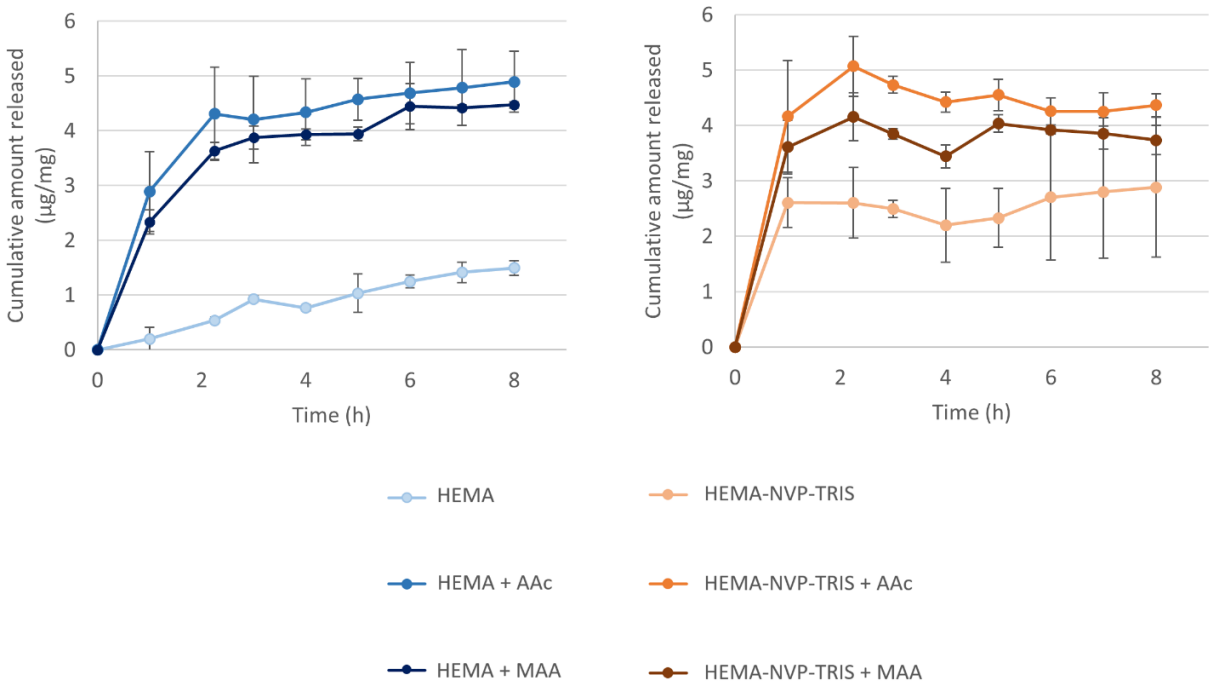

Figure 1. Cumulative amount of KTP-NH2 released from HEMA, HEMA-AAc and HEMA-MAA hydrogels (left) and HEMA-NVP-TRIS, HEMA-NVP-TRIS-AAc and HEMA-NVP-TRIS-MAA hydrogels (right). HEMA-based hydrogels (HEMA, HEMA-AAc and HEMA-MAA) could sustain the release of the peptide for 8 hours *in vitro*.

Acknowledgements

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P18

Porous materials for slow H_2S release in aqueous solution

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Since the discovery of the potential of the gasotransmitters (CO, NO and H_2S) as therapeutic agents, considerable research has been done to efficient exogenously delivering those gases. However, due to its gaseous nature, the handle, store, and appropriated delivery is hampered being necessary the development of delivery systems capable of deliver those gases to specific targeted sites in a controlled manner. In this context, porous materials have been investigated as drug delivery systems due to their high loading capacity, easy functionalization, and good biocompatibility.[1]

In this work, a glycerol-based carbon was prepared by carbonization with sulfuric acid, adapting the procedure described in literature [2], followed by thermal activation. In order to increase its biocompatibility, it was modified with chitosan using the procedure described by J. Koh *et al*.[3]. Additionally, different type A zeolites were also modified with chitosan using the same procedure.

The H_2S adsorption capacity of all the materials were evaluated using a volumetric method and its adsorption capacity compared. The H_2S release profile in aqueous solution at pH 7 was performed using the DTNB (Ellman's reagent) method and regarded as the first indication of their ability to be used as H_2S donor.

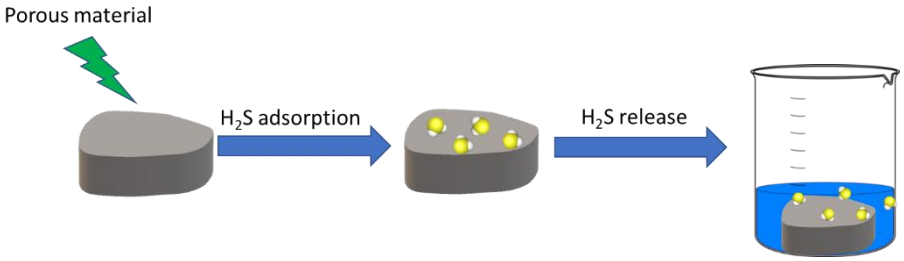

Figure 1. Schematic representation of the adsorption/release H_2S process.

Acknowledgements
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P19

Mixed hydrogenated and fluorinated ionic surfactant solutions: towards designing compartmentalized nanostructures

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Perfluorinated compounds have found significant applications in industry, such as hydrophobic coatings, packaging, refrigerants, firefighting foams and lubricants. However, their use has been under scrutiny due to their environmental impact, as they accumulate in the environment at an alarming rate, including in water basins. Thus, it is very relevant to study the behavior of these substances in water, in order to find suitable candidates for decontamination/separation processes.

Fluorinated surfactants are known to form micelles at very low concentration due to their enhanced hydrophobic character. Additionally, fluorinated chains also tend to segregate from hydrogenated chains, giving rise to interesting debates on the structure of aqueous micellar solutions containing fluorinated and hydrogenated surfactants. Indeed, the interpretation of experimental data on these systems (fluorescence[1], SANS[2] and NMR[3]) has not been consensual. While most authors agree on the large deviations to ideality of these mixed systems, some have proposed that there is intermicellar separation, while others defend that either partial or complete intramicellar segregation occurs. In this work we used atomistic molecular dynamics simulations to obtain molecular level information, which can help clarify this controversy.

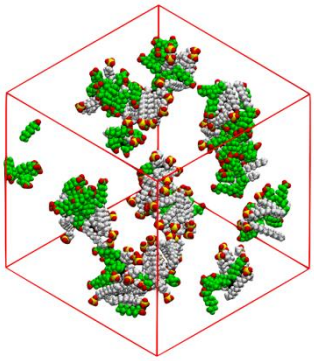

Figure 1 - Snapshot of the simulation box, showing fully formed mixed micelles.

Acknowledgements
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P20 Hybrid materials with gold nanoclusters: the future of NIR imaging

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Gold Nanoclusters (AuNCs), nanostructures with a few gold atoms, have a growing interest due to their unique properties, such as size-dependent luminescence, very high photostability, catalytic activity, low toxicity, and biocompatibility.[1] Their potential applications in different fields, from medicine and biology to physics and chemistry, include catalysis, sensing, imaging and theranostics, have been strongly explored in the last years.[2]

Our main interest in the application of AuNCs as labels for advanced optical imaging and diagnostics. The aim is the development of novel AuNCs containing nanomaterials that overcome the poor stability of isolated AuNCs. Our strategy is the incorporation of AuNCs in polymer nanoparticles through photo-miniemulsion polymerization, allowing the AuNCs to maintain their optical properties (NIR fluorescence emission) for imaging and optical targeting.

Polymer-AuNCs nanoparticles were prepared through photo-miniemulsion polymerization of methacrylate monomers, resulting in monodisperse nanoparticles with diameters around 50 nm (Figure 1A), high colloidal stability and good optical properties. The materials show emission in the NIR region, around 800 nm (Figure 1B).

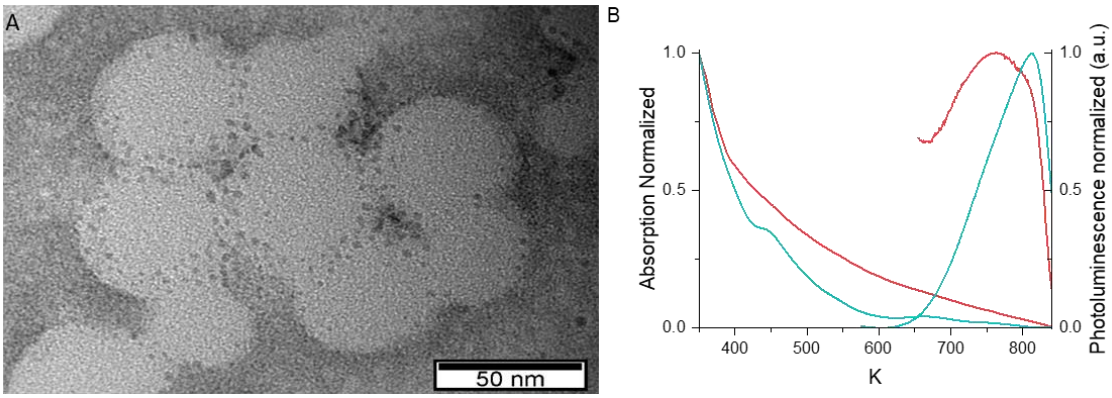

Figure 1. A) TEM image of polymer nanoparticles containing AuNCs. B) Fluorescence emission spectrum of polymer-AuNCs nanoparticles (λexc=450 nm)

Acknowledgements
This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT-Portugal) and COMPETE (FEDER), projects PTDC/CTM-POL/3698/2014, UIDB/00100/2020 and UIDP/00100/2020. B. C. thanks FCT for PhD grant PD/BD/137511/2018.

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P21

The role of stoichiometry in the stability of multicomponent crystals

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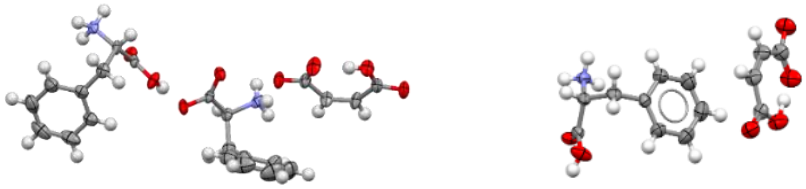
The synthesis of multicomponent crystals has emerged as a very convenient strategy to improve the physical properties of active pharmaceutical ingredients (e.g., solubility and bioavailability). A key aspect within this scope is the evaluation of the stability of the produced materials relative to their pure components, to ensure that they do not decompose during the storage period. A good indicator of that stability is the standard molar enthalpy, $\Delta_r H^o_m$, of the reaction $A_aB_b(cr) \rightarrow aA(cr)+bB(cr)$, which reflects the difference in lattice energy between the A and B precursors and the A_aB_b material. Based on this criterion A_aB_b will be stable if $\Delta_r H^o_m > 0$. An enthalpic only stability criteria can often be used because available experimental evidence suggests, that, in most cases, close to ambient temperature, $|\Delta_r H^o_m| > |-T\Delta_r S^o_m|$.[1,2]

The influence of stoichiometry on the stability of the A_aB_b materials is a virtually unexplored topic. Thus, in this work, the energetics of two organic salts consisting of maleic acid (MA) and L-phenylalanine (Phe) with 1:1 and 1:2 stoichiometries was investigated. The compounds were synthesized by mechanochemistry and structurally characterized by single-crystal X-ray diffraction (Fig.1).[3] The determinations relied on the enthalpy of solution measurements carried out with a newly developed calorimetric cell for the LKB 2277 Thermal Activity Monitor (TAM), following a previously described methodology.[1] The obtained results indicated that, at least in the present case, despite significant structural differences, $\Delta_r H^o_m(\text{MA:Phe}_2) \approx 2\Delta_r H^o_m(\text{MA:Phe})$.



(a) (b)

Figure 1. Molecular structures of (a) zwitterionic salt MA:Phe$_2$ (determined in this work),[3] and (b) MA:Phe salt (CCD reference, EDAXIQ)

Acknowledgements
This work was supported by Fundação para a Ciência e Tecnologia (FCT), Portugal (projects PTDC/QUI-OUT/28401/2017, LISBOA-01-0145-FEDER-028401, UIDB/00100/2020, and UIDP/00100/2020).

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P22

Langmuir films of ionic liquids: mono and multilayers of [$C_n$mim][X] n = 18, 20, X = NTf_2^-,Cl^- at the air-water interface

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Room-temperature ionic liquids (IL) have received a rapidly increasing interest as a new type of fluids and a promising environmentally friendly alternative to conventional solvents, to be used in a large number of applications. Many of these applications involve processes that take place at interfaces, either at the liquid-vapour interface of a pure IL or solution, or at the liquid/solid interface between an IL and a solid surface. The study of the interfacial properties of ILs, pure or in solution, is therefore of utmost importance for the development of these technological applications, since their properties can be significantly different from those of the bulk liquids. Despite its importance, the knowledge of the structural properties of ILs at the air/water interface is still quite poor. A better understanding of the behaviour of ILs at this interface can be obtained studying the formation of thin films through the Langmuir and Langmuir-Blodgett techniques. To date this is a largely unexplored field.

In this work we have studied the behaviour of films of ILs of the methyl-imidazolium family at the air-water interface using a Langmuir trough. The films were characterized by Brewster angle microscopy (BAM), Grazing Incidence X-ray diffraction (GIXD) and X-ray reflectometry (XRR). In the case of [C_{18}mim][NTf_2] and [C_{20}mim][NTf_2] we have direct evidence of the formation of mono and multi layers of these ILs at the air-water interface. Molecular Dynamics simulations provide a molecular level interpretation of the experimental results [1].

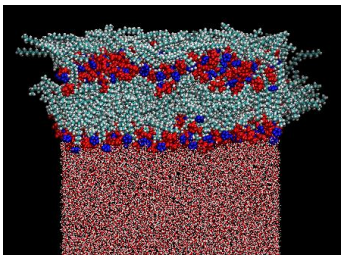

Figure 1. Simulation snapshot (side view) of a Langmuir film of [C_{20}mim][NTf_2] at 0.24 nm^2/molecule.

Acknowledgements
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P23

Tetracoordinate 9-borafluorenyl and diphenylboranyl complexes of 8-hydroxyquinolinate chelating ligands: synthesis and photophysical properties

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There has been a growing demand for organic light-emitting diodes (OLEDs), for display and lighting applications, due to their low-cost manufacturing and high energy efficiency, impacted on the search for highly performance emitter materials such as those exhibiting thermally activated delayed fluorescent (TADF) [1].

Over the past few years, our group has been involved in the synthesis of several luminescent tetracoordinate organoboron complexes containing 2-iminopyrrolyl moieties, with diverse electronic and steric features, and its influence on their optical properties, namely in fluorescence [2].

Herein, we report a group of new tetracoordinate boron complexes, containing the 9-borafluoren-9-yl and diphenylboranyl cores attached to orthogonal 8-hydroxiquinolinates ligand chromophores. The resulting design was thought to provide orthogonality between the two planar chromophores, a geometrical requirement to achieve delayed fluorescence [3]. The boron compounds were prepared by coordinating different mononegative substituted 8-hydroxyquinolinate bidentate ligand chromophores to the above-mentioned moieties (Figure 1). Their molecular structures and photophysical properties, in solution and solid state, are presented and extensively studied.

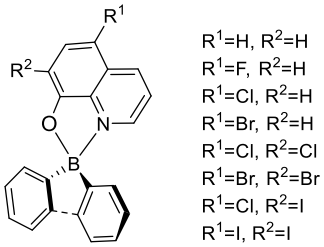

Figure 1. New tetracoordinate substituted 8-hydroxyquinolinate boron complexes.

Acknowledgements

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P24

Lyotropic ionic liquid crystal gels – molecular dynamics simulations and xenon NMR spectroscopy

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Ionic liquids (ILs) are usually defined as molten salts with melting points below 100 ºC. ILs show a variety of properties and structures, resulting from the countless possible cation-anion combinations. ILs are thus the ideal choice for a panoply of challenging applications. Some imidazolium-based ILs, such as the [$C_n$mim]X (n=8, 10; X=Br^-, Cl^-), are known for their self-assembly capabilities, in particular to form micelles and vesicles in aqueous solution [1]. Additionally, these ILs are known to form liquid crystals and gels upon addition of the appropriate amount of water. Liquid to gel transitions are accompanied by an extremely large increase of viscosity and have been observed within a narrow range of IL/water concentrations. Moreover, a variety of structures have been proposed for the gel phase depending on the water content [2, 3].

The xenon atom is in many aspects the perfect molecular probe. Moreover, ^{129}Xe NMR spectroscopy is a powerful technique to provide information on the structural properties of a range of systems, including ILs [4].

In this work, the self-assembly and the gelation potential of systems containing [$C_n$mim]X and water were investigated. MD simulations, X-ray diffraction and ^{129}Xe NMR spectroscopy were performed for pure ILs and their aqueous mixtures. The results clarify the supramolecular structures of the gel phase and the role of the water molecules, the nature of the anions and the chain length of the cations.

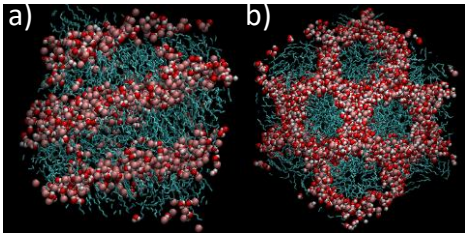

Figure 1. Snapshots from MD simulations of [C_{10}mim]Br with water in the proportions of a) 1:1 and b) 1:4.

Acknowledgements
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P25

Microporous and mesoporous materials as H_2S donors

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Hydrogen sulphide (H_2S) was the last recognized gasotransmitter, joining CO and NO into the gasotransmiter family.[1] It is well-known that exogenous H_2S delivery has therapeutic application in blood pressure reduction, cytoprotection effect, wound healing, regulation of inflammation, inhibition of insulin signalling, etc. [2] However the main challenge remains the development of donors capable of delivery H_2S at specific sites with effective concentration over a required period. Most of the existing donors have a rapid release and excessive H_2S production as observed for the sulphide salts (NaHS and Na_2S), others such as dithiolthiones, N-Benzoylthiobenzamides, S-Aroylthiooximes, have slower release rate however due to the donor degradation toxic by-products may be formed.[3] The lack of specificity is transversal to all existing donors. thus, limiting their biological application. Therefore, new materials and technologies to store and target-deliver H_2S in biological amount are required.

Here, microporous titaniosilicates (ETS-4 and ETS-10), microporous zeolites (4A and Y), and mesoporous silica (SBA-15, SBA-15 functionalized with primary [3-aminopropyl-triethoxysilane (APTES)] (APTES@SBA-15) and a diamine containing primary and secondary amine groups [N-[3-(trimethoxysilyl) propyl] ethylenediamine(N-3)] (N3@SBA-15)) are proposed as possible carriers for H_2S storage and delivery. The H_2S adsorption capacities were obtained by volumetric method and the H_2S release in liquid phase was evaluated using two different methodologies (methylene blue reaction and selective electrode). Additionally, no significant toxicity was observed for HeLa cells except for N3@SBA-15, while ETS-4 and APTES-SAB-15 were toxic for HEkn cells.[4]

Considering the storage amounts, the release profile and cytotoxicity zeolite 4A and titanosilicate ETS-10 showed the most promising results.

Acknowledgements

The authors acknowledge Fundação para a Ciência e a Tecnologia through projects PTDC/MEDQUI/28721/2017, CERENA - UID/CTM/50011/2019, CQE - UIDB/00100/2020 and UIDP/00100/2020, and CICECO – FCT UID/CTM/50011/2019.

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P26

Structurally novel nucleoside and nucleotide analogs of potential therapeutic interest

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Synthetic nucleosides, nucleotides and their analogs or mimetics have attracted considerable interest in medicinal chemistry, owing to their propensity to display a variety of bioactivities.

Their relevance in anticancer and in antiviral drug research is well demonstrated by the variety of compounds which are effective drugs, acting by interference with nucleic acid biosynthesis [1]. Their clinical use has however some drawbacks such as low cell membrane permeability and the acquisition of chemotherapeutic resistance. A number of natural nucleosides and modified analogs display antimicrobial effects [2], while some reports showed the capability of nucleos(t)ide analogs to inhibit cholinesterases [3], which remain major therapeutic targets for Alzheimer's disease.

The development of new bioactive nucleos(t)ide-like structures that may exhibit new mechanisms of action and the exploitation of less focused therapeutic uses for these groups of molecules is therefore encouraging.

In this context, in this communication, the synthesis and biological evaluation of novel nucleosides and nucleotide analogs constructed on D-glucuronamide, azido glycosyl or xylofuranose templates is presented. The groups of synthesized molecules included D-glucuronamide-based furanosyl and pyranosyl nucleosides, isonucleosides and isonucleotide mimetics. N-Heteroaromatic motifs such as purine, uracil and triazole units and potential neutral bioisostere moieties for a phosphate system were installed in the structures. The synthetic strategies involved N-glycosylation, azidation, "click" 1,3-dipolar cycloaddition, Mitsunobu coupling or Staudinger-type reaction as key steps. Bioactivity assays revealed some molecules displaying potent antiproliferative effects in cancer cells or exhibiting effective inhibition of acetylcholinesterase. Their GI_{50} or K_i values were in the micromolar concentration range, similar or close to those of standard drugs, qualifying them as prospective lead compounds for cancer or Alzheimer's disease.

Acknowledgements

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P27

Silver(I) complexes containing different bipyridine and phosphane-based ligands as potent anti-cancer agents

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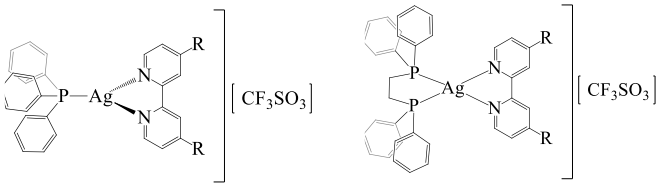
Carboplatin is one of the most important agents against ovarian carcinoma in clinical use. However, rapid occurrence of drug resistance is a major obstacle to treatment and the development of new drugs to treat tumors with acquired resistance is of high interest.

In this frame, the value of silver-based compounds as metallodrugs suitable to treat resistant cancers was proposed recently with Ag(I) compounds containing different carbene ligands that showed a high potential against cisplatin-resistant ovarian cell lines (A2780R and CP70) compared to cisplatin-sensitive cells (A2780), probably by inhibition of thioredoxin reductase [1,2].

In this work, a new family of silver(I) complexes with general formula [Ag(4,4'-R-2,2'-bipyridine)(L)][CF_3SO_3], where R = H, CH_3, CH_2OH or CH_2Biotin and L = triphenylphosphane (PPh_3) or 1,2-bis(diphenylphosphino)ethane (dppe), has been developed. All compounds were thoroughly characterized by NMR, ESI-MS, UV-Visible, FT-IR and X-ray diffraction of single crystals. Their cytotoxic activity was tested in two cell models for ovarian carcinoma with acquired resistance against carboplatin and compared to their chemosensitive counterparts by MTT assay. The preliminary data indicate that the new Ag(I) compounds are able to overcome carboplatin resistance.



R = H	(**1**)	**R** = H	(**5**)
R = CH_3	(**2**)	**R** = CH_3	(**6**)
R= CH_2OH	(**3**)	**R**= CH_2OH	(**7**)
R = CH_2Biotin	(**4**)	**R** = CH_2Biotin	(**8**)

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

Acknowledgements

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P28

Anion and ion-pair recognition by hexahomotrioxacalix[3]arene-based receptors bearing naphthyl (thio)urea groups

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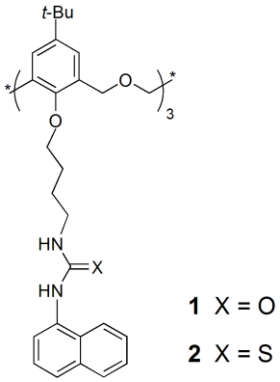
The development of synthetic receptors for the complexation of anions is still a strong research area in supramolecular chemistry due to the recognized importance of anions in biological and environmental areas.[1] The versatile macrocyclic compound calixarenes have been widely used as anion receptors. The introduction of (thio)urea units in the macrocycle scaffolds provides receptors that use mainly NH groups as hydrogen-bond donors to interact with the anions. By other side, calixarenes with fluorophoric groups have been studied due to their optical sensing ability for a large scale of analytes.[2]

Following our previous studies on anion and ion-pair recognition by dihomooxacalix[4]arene-ureido derivatives,[3,4] we have extended our research into the study of fluorescent hexahomotrioxacalix[3]arene-based receptors. This work reports the host-guest properties of compounds **1** and **2**, bearing naphthyl (thio)urea groups on the lower rim, towards several relevant anions and also *n*-alkylammonium chlorides. These studies were performed by proton NMR, UV-Vis absorption and steady-state fluorescence titrations in different solvents.



1 X = O

2 X = S

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P29

Biobased polymeric films for drug delivery systems

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Due to an imperative need to reduce our dependency on petrochemical fuel, society is making significant efforts to move toward a biobased and circular economy and the plastic sector is one of the most affected. Nowadays bioplastics can be found in several market segments and have been widely used for various purposes, including packaging, food industry, agriculture, cosmetics and medicinal applications [1]. The pharmaceutical and medical devices industries followed the trend and today many biodegradable and biocompatible macromolecules or natural biopolymers are used for medical applications such as implants, films for tissue and organ repair, sutures, surgical treads, and drug delivery systems [2]. Biocompatibility and nontoxicity are key properties of polymers used in medical applications. The present study reports the potential use of Shellac resin and Plant-based UV Eco-Resin as a controlled release matrix for drug delivery (Figure1). Produced films were dopped with acetaminophen and tetracycline as active pharmaceutical model compounds. Structure, mechanical and drug controlled-release characteristics were evaluated. It was found that tetracycline release in comparison to acetaminophen was quite low in both bio-based materials. Shellac resin films presented more elastic properties compared to Plant-based UV Eco-Resin films and dissolution profiles revealed that release rate occurs within the first 6 hours, for all hybrid materials. These preliminary results are very promising for the developing of new environmentally friendly hybrid materials, produced from natural biopolymers, as new candidates for drug delivery systems.

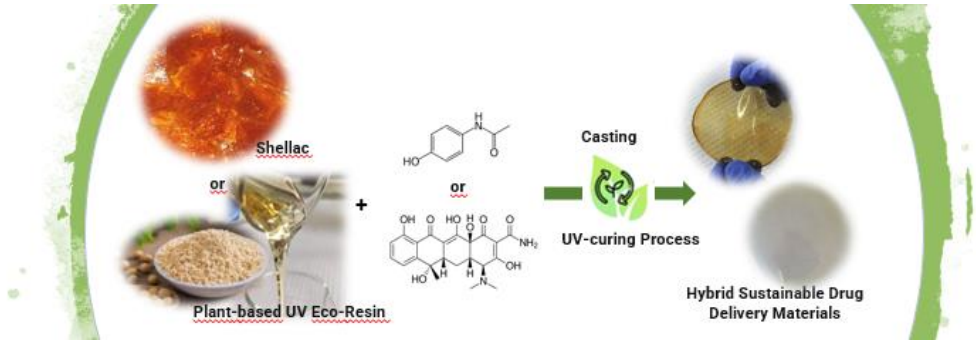

Figure 1. From biobased raw materials to innovative hybrid sustainable drug release materials.

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P30

Mass spectrometry-based Adductomics tools towards the differential diagnosis of arterial hypertension

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Arterial hypertension (HTN) impacts more than 1 billion people worldwide with major consequences in health, society, and economy. Accounting for more than 9 million deaths annually, HTN constitutes a major cause of premature death worldwide, as a leading cause of heart and kidney failure. Resistance to treatment (RHTN) constitutes a major problem for HTN management and the leading cause of HTN-related morbidity & mortality.[1]

Elevated levels of specific endogenous metabolites are recognized as a main risk factor for RHTN. Therefore, a large percentage of the population would benefit from efficient management of the adverse effects promoted by these metabolites. However, the accurate determination of RHTN-related metabolite's levels in biological samples, accessible by minimally invasive procedures, remain a major diagnostic challenge, which reflects the inefficacy of current analytical tools in assessing/mirroring the tissues levels of these metabolites.

Grounded on the hypothesis that the covalent adducts formed between HTN-related metabolites and blood proteins are better surrogates of the levels of these metabolites in tissues than their free serum levels, this work is aimed at the development of a robust and efficient Mass Spectrometry(MS)-based pipeline for the differential diagnosis of HTN.

We report herein the preliminary results obtained on the preparation and structural characterization of adducts standards along with in the optimization of a pre-analysis procedure that consist of the use of specific probes for the enrichment of covalent adducts formed between HTN-related metabolites and Human Serum Albumin. These constitute key steps towards the adequate identification/quantification of these prospective HTN biomarkers in biological samples in a clinical context. These methodologies will be subsequently tested on a cohort of HTN patients with distinct comorbidities to investigate if adducts signatures can differentiate HTN patients.

Acknowledgements

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P31

Centrosomal protein TBCCD1 as a regulator of kinetochore proteins and cell division

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Centrosomes consist of a pair of centrioles surrounded by the pericentriolar matrix that nucleate/organize the cytoskeleton and are implicated in cell migration, adhesion, and polarity, while during mitosis they assist spindle pole formation (1). Mutations in genes encoding centrosome components and regulators lead to various human disorders, including cancer and ciliopathies. Published work from our group identified a new centrosomal TBCC domain-containing human protein (TBCCD1) involved in centrosome correct positioning and primary cilia assembly (2). More recent work from our group identified two splicing variants in TBCCD1 with two very distinct interactomes. While TBCCD1 variant 1 has a large interactome enriched in centrosome/cytoskeleton related proteins, variant 2 has a smaller interactome that includes inner kinetochore proteins CENP-H and CENP-M, which have been found upregulated in different types of tumors. Therefore, this work aims to study the interaction between the kinetochore proteins CENP-H/M and TBCCD1 to assess its role in cellular division and, consequently, tumorigenesis. To do that, we are using non-tumoral and tumoral cell lines and manipulating the expression levels for TBCCD1 variants 1 and 2.

In the present work, using immunofluorescence assays we observed for the first time CENP-H at interphase centrosomes, being this localization more frequent in 293T and RPE-1 cells overexpressing TBCCD1 (Fig.1A). By Western Blot we observed that TBCCD1 overexpressing cells have lower CENP-M expression when compared to RPE-1 cells, while the 293T tumoral cells present the higher expression levels of CENP-M (Fig1B). These results seem to indicate that TBCCD1 may regulate kinetochore proteins and the cell cycle's progression. Moving forward, we intend to overexpress TBCCD1 variant 2 and study its impact in CENP-H/M. We are also using the CRISPR/Cas9 technology to generate knockouts for both variant 1 and variant 2 and then perform similar studies in the absence of TBCCD1.

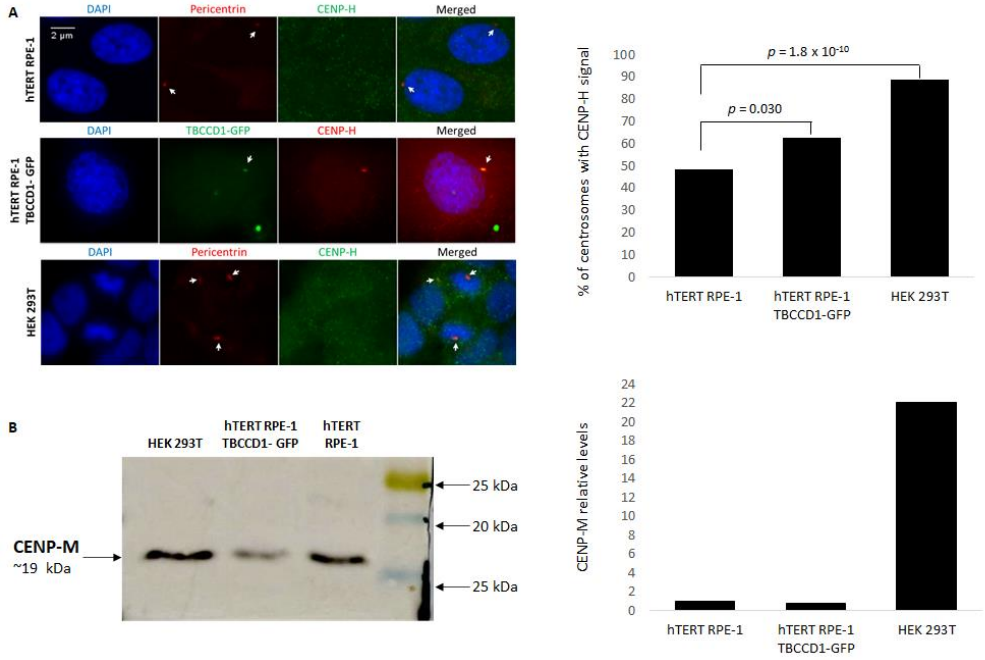

Figure 1. (A) CENP-H locates in the centrosome. CENP-H was detected in the centrosomes (arrows) in RPE-1, RPE-1 constitutively expressing TBCCD1-GFP and 293T cell lines by immunofluorescence microscopy. The localization of CENP-H in the centrosome is significantly increased in RPE-1 overexpressing TBCCD1 and 293T tumour cells. **(B)** Western-Blot analysis of total protein extracts shows that CENP-M is more abundant in tumour 293T cells and less abundant in TBCCD1 overexpressing RPE1 cell line.

Acknowledgements

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P32

Lipophilicity evaluation of new isoniazid derivatives with potential antitubercular activity

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Tuberculosis (TB) still kills three people every minute, although it is, mostly, a preventable and treatable infectious disease. A recent media brief from Stop TB Partnership stated that 12 months of COVID-19 eliminated 12 years of progress in the global fight against tuberculosis due to a dramatic decline in TB diagnosis and treatment [1]. If to this scenario we add the well documented fact that *Mycobacterium tuberculosis* (*Mtb*), the causative agent of TB, has over the years been developing increasing resistance to rifampicin and isoniazid (INH), the two most powerful first-line antitubercular drugs [2], it results obvious that it is increasingly urgent the search for more efficient and less toxic new drugs to fight this disease.

In previous works we have proven that our QSAR-oriented design departing from the INH scaffold was able to provide very promising compounds, some of which were shown to succeed in overcoming resistance to INH in the most frequent *Mtb* mutation, the *katG* S315T [3].

In this new project, we have used various *in silico* approaches to propose new sets of compounds with improved trafficking and reactivity profiles that are now being gauged from various perspectives. It is well-know that lipophilicity assessment is one of the mandatory steps in every pre-screening protocol since it gives us some information on the compounds' ability to permeate biological membranes. Therefore, in this work we have evaluated the octanol-water partition coefficient, log $P_{o/w}$, for two new series of compounds using the shake-flask method, following solubility and stability studies in both sampling phases. Interestingly, a parallel investigation within the scope of this project has revealed that most lipophilic compounds interact more strongly with human serum albumin than INH itself.

Acknowledgements

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P33

[Ru(CpR')(PPh3)(bipy-R)]+ family of compounds: prospective anticancer metallodrugs with a promising large spectrum of activity

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Every sixth deaths in the world are caused by cancer, making it the second leading cause of death (second only to cardiovascular diseases). The basis of cancer therapy is chemotherapy, but the drugs in clinical use, like the metallodrug cisplatin, still present major limitations such as non-selectivity and resistance to therapy, both responsible for serious side effects and treatments' failure. Thus, the discovery of new and selective anticancer agents, capable of overcoming these problems, is critical.

Ruthenium complexes are nowadays considered promising alternatives to the metal-based drugs in clinical use, and some have already reached the clinical trial phases, namely NAMI-A and KP1019/KP1339.[1] In this frame, the Organometallic Chemistry Research Group from CQE-FCUL has been contributing to the pioneering role of the ruthenium organometallic based compounds as selective and potent anticancer agents. In particular, we recently uncover that compounds from the [Ru(CpR')(PPh$_3$)(bipy-R)][CF$_3$SO$_3$] family, where Cp = η^5-cyclopentadienyl and R = CHO or CH$_2$OH, exhibit a strong activity against cisplatin-resistant NSCLC cells (A549, NCI-H228 and Calu-3).[2] Importantly, their mechanism of action was related to the inhibition of two ABC transporters, namely P-gp and MRP1, which are key players in cancer multidrug resistance.[2]

In this work we were interested in understanding if the potential of this family of compounds could be extended to other cancer cell lines, namely two breast carcinoma cell lines (MDA-MB-231/triple negative and MCF-7/hormone-dependent and two colorectal cancer cell lines (SW480 and RKO) and how this could be related to the expression of ABC transporters. In addition, the metabolic and plasma stability of some compounds has been also determined by mass spectrometry techniques.

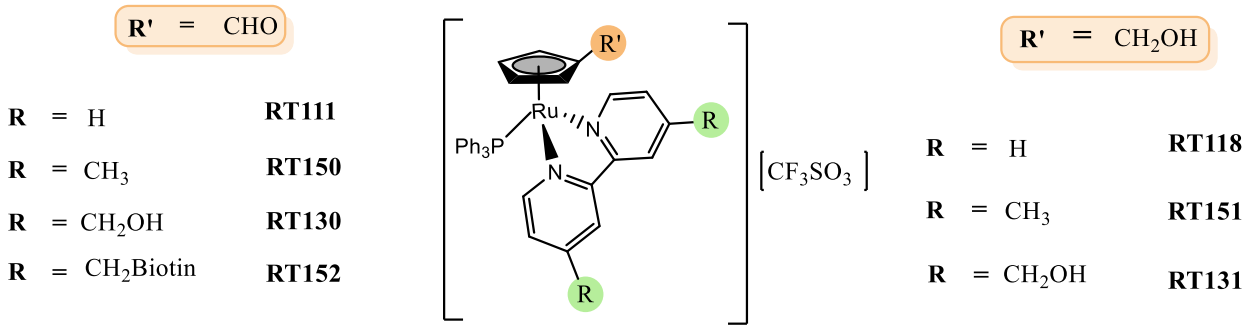

Figure 1. Chemical structures of the compounds studied from the family [Ru(CpR')(PPh$_3$)(bipy-R)][CF$_3$SO$_3$].

Acknowledgements

The authors thank the Portuguese Foundation for Science and Technology (Fundação para a Ciência e Tecnologia) within the scope of the projects UIDB/00100/2020 (Centro de Química Estrutural) and PTDC/QUI-QIN/28662/2017. RGT thanks FCT for his Ph.D. Grant (SFRH/BD/135830/2018). AV and AMM Antunes acknowledge the CEECIND 2017 Initiative (CEECCIND/01974/2017 and CEECIND/02001/2017, respectively).

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P34

Mass spectrometry-based proteomic approaches: further insights into the gender-specificity of N-Acetyl-2-aminofluorene (AAF)-induced liver carcinogenesis

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N-Acetyl-2-aminofluorene (AAF) is a model rat carcinogen. Despite similar levels of DNA adducts were identified in the livers of female and male rats exposed with AAF, there was a marked sex difference in the development and progression of GSP-positive foci (widely accepted as a morphological sign of neoplastic transformation), with the males being more susceptible. Preliminary studies (by western blot) detected decreased histone H4K20Me3 in histones isolated from the livers of male rats.[1] This observation suggests that epigenetic alterations have a role in the sex dimorphism of AAF-induced carcinogenesis. Nonetheless, the mechanisms underlying these events are yet to be elucidated.

With the ultimate goal of providing further insights into the molecular mechanisms in the onset of gender-specificity of AAF-induced liver carcinogenesis, proteins isolated from livers of male and female rats treated AAF, during 12 and 18 weeks, were analysed by mass spectrometry-based proteomics methodologies. We report herein the differential epigenetic and adductomics profiles identified in male and female samples. These results might open new avenues into the molecular mechanisms of chemically-induced cancers.

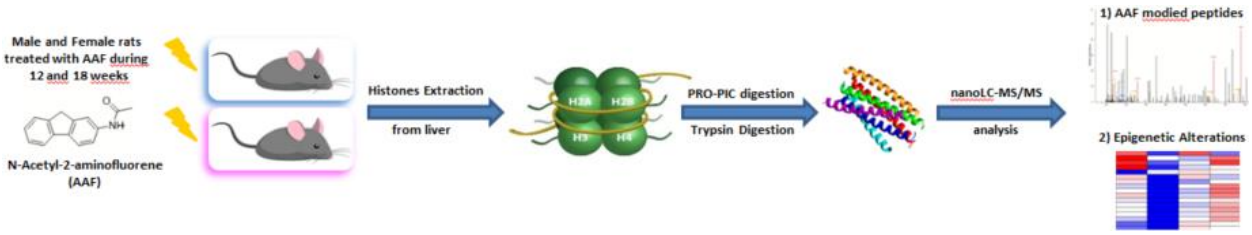

Figure 1. Experimental approach for the identification of AAF modified peptides and epigenetic changes.

Acknowledgements

The authors thank the Portuguese Foundation for Science and Technology (Fundação para a Ciência e Tecnologia) within the scope of the projects UIDB/00100/2020 and UIDP/00100/2020 (Centro de Química Estrutural) and PTDC/QUIQAN/32242/2017. JPC Nunes thanks FCT for his Ph.D. Grant (SFRH/BD/140157/2018). AMM Antunes acknowledge the CEECIND 2017 Initiative (CEECIND/02001/2017). This work was funded by an EU2020 EPIC-XS grant.

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P35

Psychoactive cathinones: metabolite profile by high resolution mass spectrometry

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Synthetic cathinones represent the second largest class of new psychoactive substances (NPS) reported worldwide and constitute a serious public health risk. In fact, the increased number of acute intoxication and deaths associated with the consumption of cathinones has resulted in their continuous inclusion in the International Drug Control Convention, based on their risk assessment. Nonetheless, one of the biggest challenges created by the rapid spread of new cathinones on the illegal drug market is the discovery of selective biomarkers for their detection in biological matrices, which is only possible through the study of their metabolic profile.

With the ultimate goal of contributing for a proactive response in tackling the NPS problem, and within the scope of a protocol established between the Forensic Science Laboratory from, Portuguese Criminal Police and the Lisbon University (Instituto Superior Técnico and Faculty of Sciences), the present work is aimed at determining the metabolite profile of selected cathinones that were already reported or that are expected to be in a near future, based on their structural similarity with other NSP.

The metabolites were generated in metabolically competent in vitro systems and were subsequently identified by Tandem High Resolution Mass Spectrometry (Figure 1).[1] The elucidation of these metabolic profiles will help not only the competent authorities to validate the consumption of these cathinones in forensic contexts but also to identify the causative agent of toxicity in clinic, thereby allowing suitable treatment.

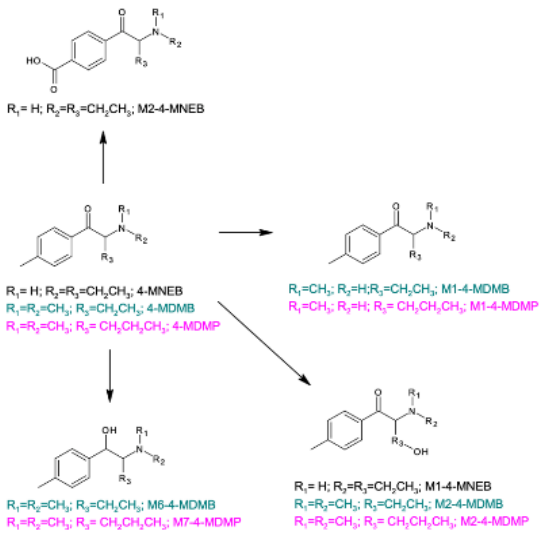

Figure 1: Metabolic Pathways Identified by High Resolution Mass Spectrometry

Acknowledgements

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P36

Enhancing the performance of Praziquantel: an approach using Crystal Engineering and Mechanochemistry

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Praziquantel (Fig. 1) is the only commercially available medicine to treat schistosomiasis in humans and is in the World Health Organization (WHO) Model List of Essential Drugs. The goal of this project is to enhance its physicochemical properties by obtaining multicomponent crystalline forms. For that, the principles of crystal engineering are being applied and mechanochemistry is the main synthetic technique used.

In the last two decades, cocrystallization has been gaining a special interest in the pharmaceutical field as it has been proved that new multicomponent crystal forms can present better properties, such as solubility and dissolution rates, than the pure active pharmaceutical ingredients (APIs).[1]

Cocrystals are homogeneous materials that contain two or more neutral building blocks in a definite stoichiometric ratio, being that these crystal forms are obtained through well-established hydrogen bonds. On the other hand, molecular salts can be formed instead of a cocrystal if the groups involved in these bonds transfer protons between acids and bases [2], leading equally to new forms with different properties.

Generally regarded as safe (GRAS) organic coformers, such as -muconic, trimesic and L-tartaric acid, were used to obtain multicomponent forms of praziquantel by mechanochemistry [3]. The structural characterization of the novel compounds by powder, and single crystal X-ray diffraction, as well as FTIR-IR is on-going. Thermal stability, solubility and antimicrobial activity of the products will be assessed.

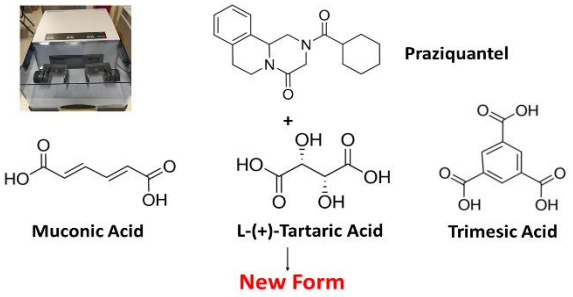

Figure 1. Schematic representation of the project.

Acknowledgements
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P37

Partition of the antifungal drug Ketoconazole and a new diphenylphosphane oxide derivative towards phosphatidylcholine lipid bilayers

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Ketoconazole (Ke) belongs to the important family of azole antifungal drugs, which act by inhibiting cytochrome P450 sterol-14α-demethylase, an important enzyme in ergosterol biosynthetic pathway [1]. However, Ke shows poor absorption and risk of liver injury when administered orally [2]. Moreover, the increased development of resistance to antifungal drugs [1] brought renewed attention to the search for more efficient antifungal agents.

Recently, new promising antifungal Ke diphenylphosphane derivatives were developed [3,4]. Although these compounds share the mode of action with Ke, the differences between the antifungal activity of Ke and its derivatives against certain strains of *Saccharomyces cerevisiae* and *Candida albicans* [4] point to additional modes of action.

The objective of this work was to determine if Ke and its diphenylphosphane oxide derivative, KeOP, interact differently with lipid bilayers to an extent that can be considered of biological relevance in the context of antifungal mode of action.

To evaluate Ke and KeOP interactions with lipid bilayers, the intrinsic fluorescence of these compounds [4] was studied in the presence of large unilamellar vesicles, prepared with different concentrations of 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), a lipid commonly found in membranes of eukaryotic organisms. An increase in the steady-state fluorescence intensity, anisotropy and blue-shift of emission of both Ke and KeOP was observed with increasing lipid concentration. This shows the interaction of these compounds with the lipid bilayer. The variation of fluorescence intensity was used to determine the membrane/water partition coefficient, K_p, for each compound.

The K_p for KeOP [$(4.66\pm0.7)\times10^6$] was ca. 14 times higher than the one for Ke [$(3.31\pm0.4)\times10^5$], indicating that KeOP interactions with the membrane are much more favorable possibly due to the presence of a hydrophobic $-CH_2P(O)Ph_2$ moiety.

These results give insight on additional modes of action of Ke and its derivatives that include the interaction with fungal cell membranes that may help in the design of novel drugs.

Acknowledgements
This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, through grants UIDB/00100/2020 and UIDP/00100/2020 (Centro de Química Estrutural), and doctoral scholarship to A.B.O. (SFRH/BD/145600/2019).

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P38

A reappraisal of the regioselectivity and specificity of bacterial-expressed cytochromes P450

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One of the most common drug detoxification pathways involves cytochrome P450 (CYP)-mediated oxidation of the parent drugs. However, this can also lead to the bioactivation of the drug, with possible toxic side effects. Using bacteria for recombinant CYP expression, aiming to develop biomimetic modules of drug reactions, presents the common drawback that electron transfer from NADPH to CYPs is inadequate, often require the co-expression of NADPH CYP oxidoreductase (POR) or addition of the purified enzyme to the reactions in order to obtain a sustained metabolite production[1].

In this work, we addressed the regioselectivity and substrate specificity of recombinant CYP isoforms 2D6 and 2C8 towards a set of substrates. We subcloned the canonical isoforms of the CYP enzymes in expression competent *Escherichia coli*, and used the recombinant proteins to metabolise various substrates. Reaction products were analysed by UPLC-ESI-HRMS/MS in order to identify which products were obtained. As control, commercially available insect-derived baculosomes co-expressing rhCYP2C8 or rhCYP2D6 with rhPOR, where post-translational protein processing is maintained, were used.

Nevirapine and tamoxifen were used as model substrates as their *in vivo* biotransformation is well studied. Using both bacteria- or insect-derived recombinant protein, nevirapine was converted to the same set of phase I metabolites, namely hydroxylated metabolites and a decyclopropyl metabolite. On the other hand, tamoxifen was found to be hydroxylated to its major *in vivo* metabolites, and was also demethylated, in agreement with the *in vivo* pathways.

These results support the use of prokaryotic cells to express recombinant human proteins for use in drug metabolism studies, without changes in the regioselectivity of enzymatic product formations nor in the enzymatic substrate specificity.

Acknowledgements
This work was funded by Fundação para a Ciência e a Tecnologia (FCT; Portugal) through projects UIDB/00100/2020, SAICTPAC/0019/2015, PTDC/QUI-QAN/32242/2017, and FCT and Portugal2020 funding to the RNEM (LISBOA-01–0145-FEDER-402–022125) MS Facility at Técnico node.

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P39

Colchicine blocks tubulin heterodimer recycling by tubulin cofactors TBCA, TBCB and TBCE

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Colchicine has been used to treat gout and effectively prevent autoinflammatory diseases and both primary and recurrent pericarditis episodes. The anti-inflammatory action of colchicine seems to result from a compromised MT cytoskeleton that affects several inflammatory pathways in cells that mediate immune response like the entire NLRP3 inflammasome [1]. Emerging results show that the MT network is a potential regulator of cardiac mechanics [2]. Here, we investigated how colchicine impacts tubulin folding cofactors TBCA, TBCB, and TBCE activities [3]. We show that the exposure of human cells to colchicine causes a decrease of the TBCA/β-tubulin complex to vestigial levels followed by an increase of free TBCA. Free TBCA was never observed in human control cells nor in cells exposed to other anti-mitotic MT depolymerizing agents, or even after translation inhibition by cycloheximide. The appearance of free TBCA is accompanied by an increase in free soluble tubulin heterodimers due to MT depolymerization. In *in vitro* assays, we show that colchicine inhibits tubulin heterodimer dissociation by TBCE/TBCB, affecting heterodimer recycling/quality control. Together our results suggest that MT depolymerization by colchicine treatment is not only due to the conformational alteration of the tubulin heterodimer but also to the inability of cofactors to recycle these heterodimers, which also explains the irreversible colchicine action. Alteration of TBCA levels, either by RNAi or by overexpression, causes the decrease of tubulin heterodimers. These data strongly suggest that TBCA mainly receives β-tubulin from the dissociation of preexisting heterodimers instead of newly synthesized tubulins. The TBCE/TBCB/TBCA triad is also crucial for controlling the critical concentration of free tubulin heterodimers and MT dynamics in the cells by recycling the tubulin heterodimers. The finding that colchicine affects the tubulin heterodimer recycling/degradation system TBCE/TBCB+TBCA should be considered in the context of colchicine's therapeutic benefits as an anti-inflammatory drug.

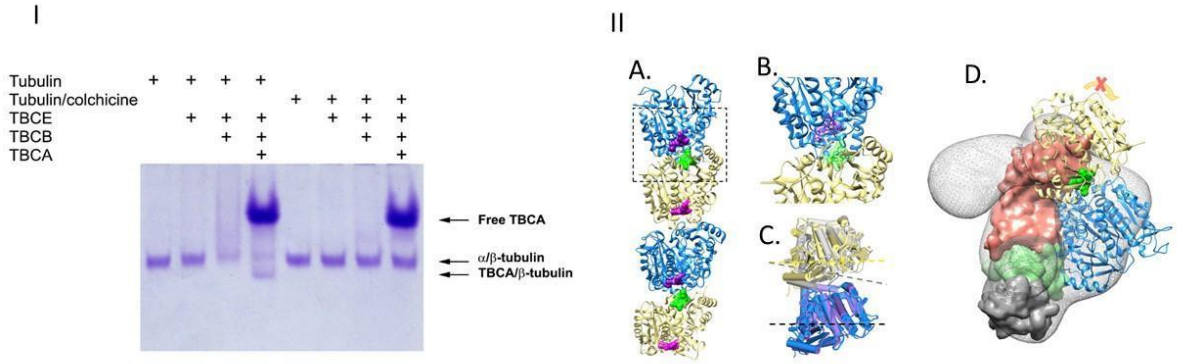

Figure 1. TBCB/TBCE complex cannot to dissociate the tubulin-colchicine heterodimer which leaves TBCA free (I) probably impairing TBCE-TBCB complex function in the α/β-tubulin heterodimer dissociation process by stabilizing the α-tubulin/β-tubulin interface (II). (I) Purified tubulin and tubulin-colchicine heterodimers were incubated with or without TBCE, TBCB and TBCA, according to the table, to perform tubulin heterodimer dissociation assays. The tubulin heterodimer dissociation assays were analyzed by non-denaturing gel electrophoresis and stained with Coomassie brilliant blue. When colchicine is bound to tubulin, TBCE and/or TBCB cannot dissociate the tubulin heterodimer. Consequently, in the presence of TBCA, we did not detect the presence of the TBCA/β-tubulin complex. Colchicine impairs the tubulin dissociate activity of TBCE/TBCB, leaving TBCA free. (II) (A) α/β-tubulin heterodimers stabilized by the colchicine molecule (green surface). The GTP/α-tubulin and the GDP/β-tubulin blue and yellow, respectively; GTP and GDP surfaces are shown in purple and magenta, respectively). (B) Zoom-in view of colchicine (green) at the α/β-tubulin interface, next to the α-tubulin GTP binding pocket. The presence of colchicine affects the α/β-tubulin interface geometry, as shown with the dash lines. (D) The complex TBCE-TBCB, hold by the interaction between the CAP-Gly domains (TBCE CAP-Gly domain surface in green and TBCB CAP-Gly domain surface in gray), binds the α-tubulin monomer of the α/β-tubulin heterodimer (blue) pushing the TBCE LRR domain toward the β-tubulin monomer (yellow) and distorting the α/β-tubulin interface. The presence of colchicine (green surface) could impair α/β-tubulin heterodimer dissociation by stabilizing the α/β-tubulin interface, making it resistant to the mechanical force applied by the LRR domain.

Acknowledgements

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P40

Drug-eluting casein hydrogels for wound dressings

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Drug loaded hydrogel dressings are considered promising candidates for the treatment of different types of wounds. They present a 3D-structure that mimics the skin extracellular matrix, namely in what concerns the water content, being able to ensure a moist environment to the wound.

The present work aims to develop drug-eluting casein-based hydrogels for wound dressings. Due to their biocompatibility, mechanical properties, ability to interact with soft biological tissues, and presence of many functional groups susceptible to chemical modifications, they have been used in a vast range of biomedical applications, including wound dressings [1].

Hydrogels were prepared through free radical polymerization of acrylamide and coagulation of casein micelles. The solution was poured into a glass mould, exposed to UV for 4h and then left for 22h at 36ºC for casein gelation.

The hydrogel's swelling was assessed in water and in both drug solutions, Octiset® (1mg/mL of octenidine dihydrochloride and 20mg/mL of 2-phenoxyethanol) and polyhexanide (0.5mg/mL). Mechanical behaviour was studied through tensile tests on hydrated samples. After drug loading, the release kinetics was obtained in sink conditions in PBS at 34ºC and 180 rpm. Sterilization was carried out in autoclave at 121ºC for 20 minutes. Antimicrobial properties against *S.aureus* and *P.aeruginosa* were also studied.

The hydrogels showed high values of swelling, 2100% in water and 1038% and 992% in Octiset ® and in polyhexanide, respectively. Tensile tests led to a Young module of 0.0156MPa. Polyhexanide loaded samples were able to release the drug in a controlled way during 48h (Figure 1), in contrast with the ones loaded with Octiset®, which led to a burst release. The drug-loaded hydrogels showed good antimicrobial properties. Further investigation to improve the release profiles of the Octiset® components is under way.

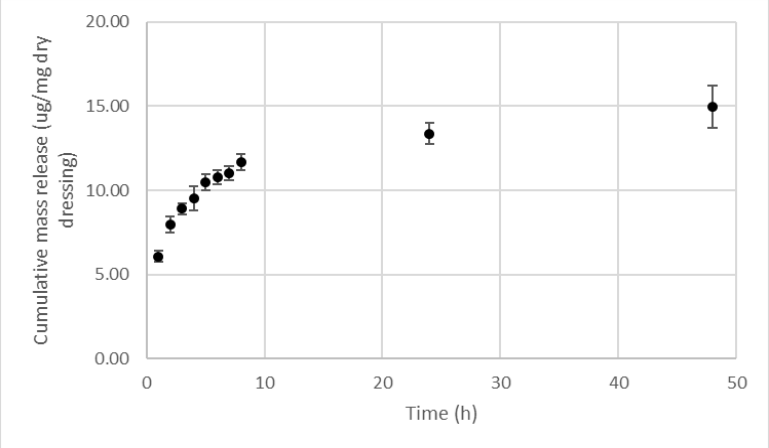

Figure 1. Cumulative drug release of polyhexanide from the produced casein-based hydrogels.

Acknowledgements
The authors acknowledge to Fundação para a Ciência e a Tecnologia for the financial support (grant numbers: UIDB/00100/2020 and UIDP/00100/2020).

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P41

Prevention of PAINS-promoted membrane perturbations via C-glycosylation: a new strategy to put natural polyphenols back in the game of drug discovery

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Since Pan-Assay Interference CompoundS (PAINS) were firstly described as promiscuous molecules capable of interfering with high-throughput screening results, concerns have been raised when it comes to investing in natural polyphenol scaffolds as leads for further development.[1] Despite promising bioactivities in cell-free assays against protein targets with therapeutic interest for cancer, diabetes, and Alzheimer's disease, genistein (1) and resveratrol (2) are two good examples of planar compounds that are believed to display membrane-perturbing effects ultimately leading to subtle alterations in the conformation and function of transmembrane proteins.[2] In this work, we show through fluorescence ratiometric measurements that phloretin (3), genistein (1) and resveratrol (2) act by decreasing membrane dipole potential, especially in cholesterol-rich domains such as lipid rafts, which play a role in important cellular processes. These results provide a mechanism for their labelling as PAINS through their ability to disrupt cell membrane homeostasis.[3] Furthermore, we present the first synthesis of glucosylresveratrol (5) and demonstrate that polyphenol-promoted membrane dipole potential alterations are fully prevented upon C-glucosylation, which brings new opportunities for the exploration of glucosylpolyphenols as leads for drug development without the risk of false positive results associated with membrane-disrupting effects.[3] The most likely biophysical mechanisms by which the sugar moiety is able to protect the cell membrane will also be rationalized and discussed in this communication.

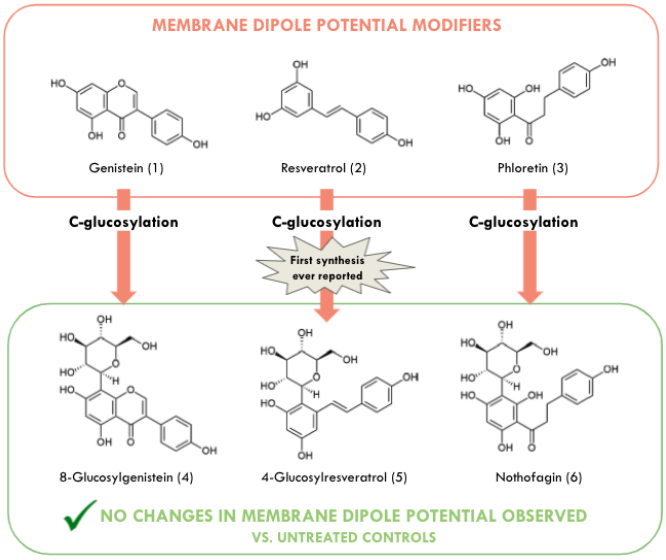

Figure 1.

Acknowledgements
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P42

Development of an immunosensor for gout monitorization in the academic population: Optimization of the bioreceptor immobilization procedure

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Gout is a clinical syndrome characterized by joint inflammation due to high levels of uric acid in blood from excessive intake of meat, fish and shellfish, which accumulate in these systems as crystals of sodium urate [1]. The diagnosis is typically performed by microscopic and imaging techniques which are expensive, laborious and time consuming. Therefore, our group is developing an alternative methodology, in particular a piezoelectric immunosensor [2], for early acid uric determination in urine and blood, characterized by simple operation, quick response, possible reutilisation and low cost. One of the most important aspects in developing and assembling a biosensor concerns the immobilization of the bioreceptor on the transducer surface. In this project the bioreceptor consisted of antibodies against uric acid immobilized on the surface of a gold electrode covering a 14 mm diameter quartz crystal. For this procedure we prepared a 11- Mercaptoundecanoic acid (MUA) Self Assembled Monolayer (SEM) on the surface of the sensor, followed by activation of carboxyl groups using a mixture of N-Hydroxysuccinimide (NHS) and N-(3-Dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC). The antibodies were added to the treated surface and covalently immobilized by an amide bond between the antibody amino groups and the activated carboxyl groups. After this incubation step, the remaining active carboxyl groups were neutralized with ethanolamine (ETA) and non-specific interaction minimized with bovine serum albumin (BSA) [3]. The optimization assays concerning the immobilization methodology included the effect of MUA, EDC, NHS, antibody, ETA and BSA concentrations, the incubation time used in every step of the process, the procedure for sensor surface modification (namely dip coating and drop casting) and the temperature effect on antibody incubation. A correct immobilization procedure is extremely important in order to obtain an adequate load of surface antibodies and also to enhance biosensor´s analytical performance, namely in what limit of detection, linear response interval, sensitivity, selectivity, precision and operational stability it concerns. The optimized biosensor device will be used to monitor the amount of uric acid in our institution's academic population and relate the results with its dietary profile.

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P43

High resolution mass spectrometry-based metabolomics: a tool for the diagnosis of inflammatory rheumatic diseases

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Early diagnosis of inflammatory rheumatic diseases (IRD), as axial Spondyloarthritis (axSpA), Rheumatoid Arthritis (RA) and Systemic Lupus Erythematosus (SLE), represents a major clinical challenge. However, increasing evidence point to early diagnosis, prompt treatment initiation and early achievement of remission as the main predictors of long-term better clinical, functional and radiographic outcomes. Therefore, the identification of differential biomarkers is key for the early detection and, therefore, for the initiation of precise therapy regimens. Given that metabolomics is a post-genomics technology that offers the closest characterization of the phenotype, this methodology can constitute a key tool for discriminating patients with IRD.

The current study is aimed at identifying differences in the urinary and plasmatic metabolic profiles and develop a feasible clinical approach for early axSpA, RA and SLE diagnosis. Towards this goal, a cross-sectional non-targeted mass spectrometry-based metabolomics study was performed in a study population composed by: axSpA (according to ASAS criteria), RA (according to ACR/EULAR criteria for RA) and SLE (according to ACR classification criteria for SLE) patients and healthy controls (HC). Patients with co-occurrence of other IRD or having received biotechnological therapies were excluded. Urine and plasma samples were analyzed by liquid chromatography high-resolution mass spectrometry (LC-HRMS) and data was subsequently pre-processed with the open-source software XCMS. The resulting matrix was normalized by total area and analyzed by multivariate analysis with the SIMCA software.

The preliminary results obtained suggest that the urinary[1] and plasmatic metabolite profiles can be helpful diagnosis tools to discriminate IRD patients in established stages of the disease and seems to provide abundant information for understanding molecular mechanisms for disease susceptibility and progression. Further studies are needed to validate these results and allow its application in clinical practice.

Acknowledgements

The authors would like to thank the Portuguese MS network for providing access to the LC-MS facilities and Fundação para a Ciência e a Tecnologia (FCT), Portugal, for funding with projects UIDB/00100/2020 and UIDP/00100/2020 (to Centro de Química Estrutural) and PTDC/QUIQAN/32242/2017. Joint funding from FCT and the COMPETE Program is also acknowledged through RNEM-LISBOA-01-0145-FEDER-022125 postdoctoral fellowship (to JM). This work was also funded by H2020 SME instrument, grant agreement 854501. AMM Antunes acknowledges the CEECIND 2017 Initiative (CEECIND/02001/2017).

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P44

Tackling multi-drug resistant tuberculosis

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Despite of COVID-19, tuberculosis is still the main cause of death from a single infectious agent, the *Mycobacterium tuberculosis* (*Mtb*), in lower-middle-income countries. Isoniazid (INH), one of two most powerful first-line drugs to fight *Mtb* infections, is part of all multi-therapeutic regimens recommended by the World Health Organization. However, mutations in the enzyme KatG have led to an increased resistance to INH. A large fraction of the new (3.3%) and previously treated (17.7%) tuberculosis cases exhibits multidrug resistance (MDR) [1] and thus it is urgent to develop new, effective and low toxicity antitubercular compounds. Previous work has enabled the synthesis of new INH-derived compounds, one of which exhibiting a 6-fold higher activity than the reference compound, INH, against the clinically most common *Mtb katG* mutated strain, S315T [2].

The main purpose of this work is to use various biophysical approaches to predict the therapeutic potential of the new compounds, and eventually contribute to the development of more efficient drugs to fight MDR tuberculosis. Given its importance for drug bioavailability, the interaction of INH derivatives with human serum albumin (HSA), including the determination of dissociation constants and the identification of the putative binding site, was investigated. Results obtained show that all compounds interact more strongly with HSA than INH, being the binding constant, in some cases, 2 orders of magnitude larger, which is in line with their lipophilicity behaviour [3]. Concomitantly, the viability of HepG2 cells was maintained for compounds' concentrations well above their minimal inhibitory concentration against *Mtb*. These encouraging results make these derivatives possible alternative molecules to be included in current therapeutic regimens against MDR tuberculosis. The interaction of the new compounds with models of the macrophage plasma membrane, lung surfactant and of the cell wall of *Mtb* is now being evaluated.

Acknowledgements

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P45

Metabolic pathway deficiencies are compensated by higher energy dissipation to maintain microbiological growth rate in Saccharomyces cerevisiae

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The development of experimental methods for earlier detection of diseases is a crucial step for improving treatment efficiency. In this work, the energy dissipation rate during cellular growth was tested as an early biomarker for metabolic perturbations. This was achieved by using calorimetry to follow the heat dissipated throughout the growth cycle of *Saccharomyces cerevisiae* (*Sc*), in media with different levels of complexity and nutrient content. By supplementing the calorimetric measurements with the determination of key cellular parameters (e.g. cell count), fundamental insights into the speed, accuracy and energy cost trade-offs associated with cell adaption to growth media were obtained.

Medium of higher complexity was observed to decrease the rate of cell adaptation to growth media (measured by the duration of the lag phase). In other words, *Sc* cells adjust their internal molecular machinery to achieve a better fitting to the environmental conditions faster if the medium components are smaller and more accessible molecules. Surprisingly, decreasing the non-carbon nutrient abundancy led to a 60% higher energy dissipation rate, but the microbiological growth was not affected with the accuracy of cell adaptation to growth media (measured by the maximal proliferative rate) remaining similar in all conditions. Thus, a higher energy dissipation rate compensates for partial nutritive limitations allowing *Sc* cells to maintain their microbiological growth rate. Supporting these observations, *Sc* cells under nutrient limitations spent a larger amount of resources in order to fully adapt to the growth medium, e.g. glucose consumption and funneling of glycolytic metabolites into other metabolic pathways increased.

In conclusion, the rate of energy dissipation is largely affected long before nutrient limitations impact the growth curve in terms of traditional microbiological measurements. Detection of this enhanced energy waste, therefore, provides a potential biomarker for metabolic deficiencies, either inborn or age-related, or triggered by pharmaceuticals or environmental xenobiotics.

Acknowledgements

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P46

Characterization of binary systems {Water (1) + Alkanolamine (2)} using different molecular probes at 293,15K, 298,15K and 303,15K

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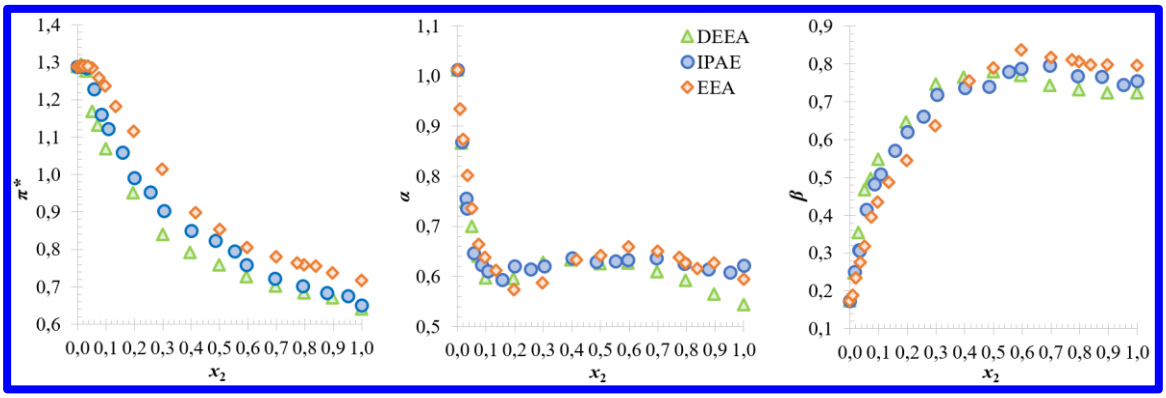
Emissions of acid gases from industrial processes inducing significant climate changes require urgent solutions to address this problem. The use of new solvents is of high interest in chemical absorption for CO_2 capture and its later release and storage. Lately the study of amines and aqueous mixtures of amines has been highly performed with the purpose of contributing to the improvement of procedures for reducing CO_2 emissions to the atmosphere[1]. In our work the microscopic solvatochromic parameters of three aqueous binary systems, 2-Diethylethanolamine (DEEA), 2-Isopropylethanolamine (IPAE) and 2-Ethylethanolamine (EEA) were determined. The Abraham-Kamlet-Taft solvatochromic parameters, polarizability/dipolarity (π^*), acidity (α) and basicity (β)[2], were obtained at the three temperatures, using some molecular probes: Reichardt Betaine 30 and 33, 4-Nitroaniline and *N,N*-Dimethyl-4-Nitroaniline. The influence of solute-solvent-solvent interactions on the preferential solvation of these indicators were also studied by applying the Elisabeth Bosch and co-workers model[3]. The characterization of the three aqueous binary mixtures based in those parameters are shown in the following figure as a function of alkanolamine mole fraction, x_2, at 298,15 K:



Acknowledgements

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P47

Effect of particle size and surface chemistry on re-use studies of activated carbons for the adsorption of methylene blue dye

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Activated carbons are excellent adsorbent materials widely applied, namely in water treatment processes [1,2]. In this work two commercial activated carbon samples from Norit (GAC) and Ingevity (D) with distinct surface chemistry properties and granulometry ranges were used as adsorbents for the removal of methylene blue (MB) dye from aqueous solutions at 30 ºC (Figure 1). MB uptake was assessed by UV-vis spectrophotometry (Jasco V530). Kinetics studies and isotherms were performed and, in the case of GAC material, the effect of particle size was assessed. Preliminary results showed that smaller particles of GAC (0.149-0.297 mm) allowed the removal of more than 90% of MB upon 4 h contact time whereas for larger particles (0.297-0.420 mm) and for the same contact time the removal was about 70% and 80% for GAC and sample D, respectively.

The reusability will be investigated using several methodologies (thermal, ultrasonic and microwave treatments) to regenerate samples after 4h of contact time. The effect of particle size and surface chemistry will be evaluated.

Figure 1. Experimental apparatus for the adsorption assays

Acknowledgements

The authors acknowledge financial support from Fundação para a Ciência e a Tecnologia, Portugal (UIDB/00100/2020). The authors also thank Ingevity Co., USA for supplying the activated carbons.

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P48

Pt loaded activated carbons as bifunctional catalysts for isodewaxing reaction

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The hydroisomerization of long chain *n*-alkanes, commonly designated as isodewaxing reaction) aims to transform high molecular weight linear hydrocarbons from the Fischer-Tropsch process into low branched molecules with good cold-flow properties that integrate the formulation of fuels and lubricants [1]. The reaction occurs in the presence of a bifunctional catalyst comprising a noble metal, that is responsible for the hydrogenation/dehydrogenation steps, immobilized in a porous support with mild acidity, which is responsible for the isomerization step (Figure 1). The most used supports are zeolites or zeotypes, generally silicoaluminophosphates (SAPOs). However, the microporous nature of these materials is responsible for the occurrence of diffusion limitations that hinders the access to the active sites located inside the pores.

In this work, two samples of activated carbons supplied by Ingevity Co. USA were used as active support for the immobilization of Pt (1 wt.%) through impregnation method with $Pt(NH_3)_4.xH_2O$ [2]. Prior to the immobilization method the surface chemistry of the samples was modified by performing oxidative treatments with HNO_3 [2]. The textural properties of activated carbons samples were characterized by low temperature N_2 adsorption, the effect of oxidative treatments was assessed through thermogravimetric essays and FTIR spectroscopy. The catalytic behaviour of the bifunctional catalysts was studied in the hydroisomerization of *n*-decane at 320-350ºC and WHSV of 6.6 and 11 h^{-1}.

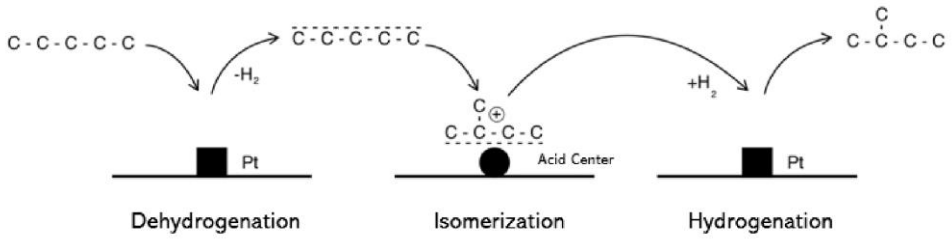

Figure 1. Simplified scheme for the hydroisomerization reaction of linear alkanes.

Acknowledgements

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P49

Plastic to Steam Cracker feedstock: A pathway to circularity

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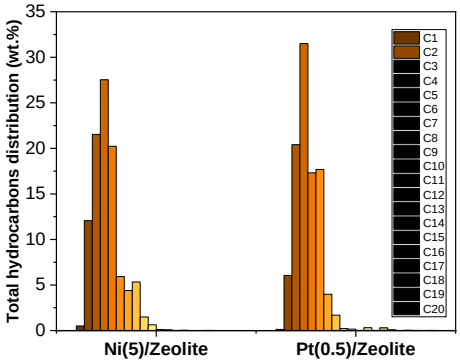
Plastic waste (PW) management poses a great challenge that must be urgently addressed. Great part of PW is still deposited in landfills or recovered by incineration, leading to environmental sustainability problems. Chemical recycling (CR) is an emerging theme in PW management which has the potential to contribute to a low carbon, resource efficient and sustainable economy[1]. As a form of CR, the hydrocracking (HDC) process is a promising route to convert PW into valuable hydrocarbons with low olefin, aromatic and naphthene contents, making them potential feedstocks to comply with the Steam Cracker (SC) process specifications (C_4-C_9 hydrocarbons, no olefins, naphthene < 16,4 %, aromatic <4.8 %)[2]. SC allows to produce ethylene and propylene monomers, closing the plastics cycle in a circular economy.

This work evaluates the potential of parent and Ni or Pt based zeolite catalysts to convert HDPE into valuable hydrocarbon feedstocks using HDC process. The influence of catalyst nature (monofunctional vs bifunctional) and metal nature on process conversion and products distribution was analyzed in this study. The possibility to reuse the metal-based systems for more than one HDC cycle was also studied. The results have shown that metal-based zeolites are promising systems to convert HDPE into a high-quality gas stream (90 wt.%), meeting the SC feedstock specifications. In addition, the Ni and Pt based catalysts proved to be efficient for more than one HDC cycle, allowing a complete conversion of HDPE and yielding a product distribution similar to the fresh systems.

Wt.%	Ni/Zeolite	Pt/Zeolite
n-parafins	5.7	5.9
i-parafins	83.6	78.4
Olefins	0.0	0.0
Naphthenes	7.4	6.8
Aromatics	3.3	8.8



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P50

Can a portable XRF be used for solution determination of metals?

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The aim of this study is to test an analytical methodology that can be useful in an industrial context by using ED-XRF spectrometry. An ED-XRF spectrometer is cheaper, has almost no operational costs compared to other analytical techniques, turning this into a fast, accessible multi-elemental analysis which is also able to process a high number of samples in a row [1]. Moreover, the developed procedure should be kept simple. It is preferable to have little sample preparation although this ought not to compromise the analytical accuracy. In most cases ED-XRF is used on solid samples. Here it will be used to evaluate the metal content of solutions by impregnating an inert matrix (in the present case cellulose) with the solution to be analysed.

The solutions used for the study were randomly generated in a determined range using mother solutions. In addition, to see if there are some interference from each other on the measurements, solutions with only one of the metals in study were also used. In this first approach Ni, Cu, Zn and Y (all elements present in the default calibration set of the equipment) were used.

The calibration correlation for Y, as an example, is presented in Figure 1, showing that the methodology can be used with success.

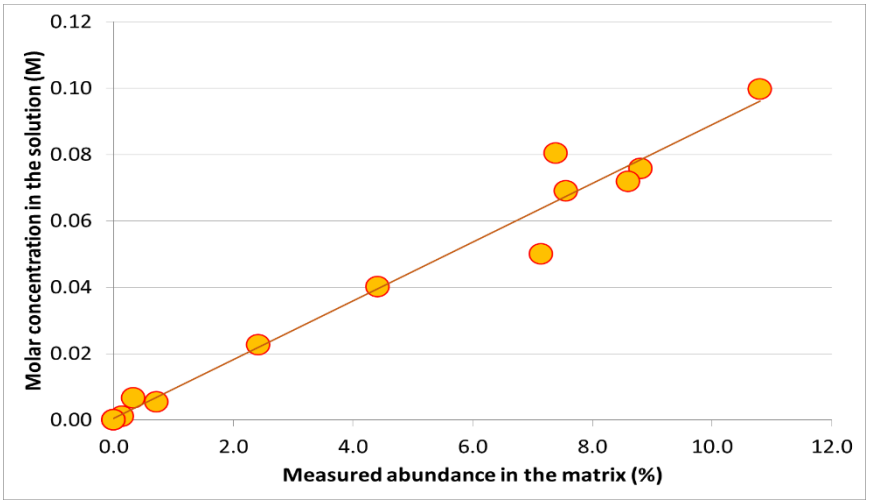

Figure 1. Calibration for Yttrium (Molar concentration = 0.0089 × Measured value + 0.0004; r = 0.973)

Acknowledgements
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P51

Simulation of the electrochemical response of cobalt hydroxide electrodes for energy storage

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Cyclic Voltammetry (CV) is an important method of electrochemical analysis, capable of revealing key characteristic behaviours by quantitative and qualitative interpretation of its curves – cyclic voltammograms. In CV, current is measured across a potential sweep which covers a forward and backward stage across a well-defined voltage window that depends on the nature of the electrode active material. The mathematical relationships between the current and voltage are dependent on other variables like electrolyte concentration, electron-transfer rate, distance to the electrode's surface, and time. It is vital to understand the mathematics between these variables to effectively relate the current with the potential. A computational MATLAB® simulation was developed [1] on the pillars of diffusion (Fick's 2nd Law) and kinetics (Butler-Volmer equations) towards simulating an approximation of the electrochemical response of cobalt hydroxide electrodes for energy storage using a point-cell calculation method. Both the capacitive and faradaic contribution of the respective processes were considered, as well as the presence of secondary reactions to the system (i.e., oxygen evolution reactions – OER). The simulation was ultimately compared to a real empirical case of the same system. The CV obtained with simulation showcased remarkable approximation to the real experimental performance with noticeable deviations possibly related to other secondary reactions and physical/chemical events that influence the diffusion and kinetics of the involved species.

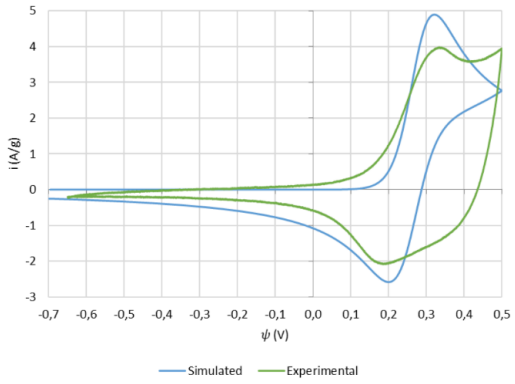

Figure 1. Comparison of simulated and experimental CV curves

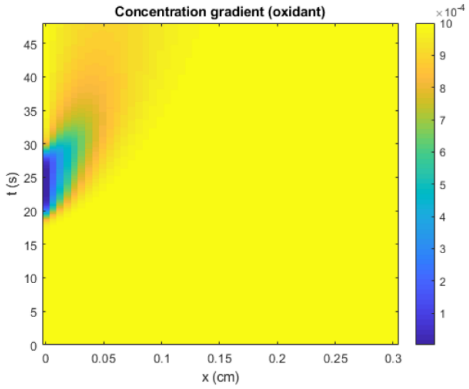

Figure 2. Simulated concentration gradient of oxidant (OH^-)

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P52

Picolinium-based Deep Eutectic Systems (DESs) in the Lubrication of Silicon Surfaces

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Deep eutectic systems (DESs) have recently been proposed as “green” alternatives to mineral oils and ionic liquids (ILs) in the lubrication of several surfaces.[1][2] DESs have similar physical properties to ILs but have the advantage of being cheaper and easier to prepare. In a previous work, we have synthesized sulphur-containing DESs that showed very interesting lubrication properties.[3] Herein, new picolinium salts-based DESs were prepared and tested in the lubrication of silicon surfaces which are relevant for nano/microelectromechanical systems (NEMS/MEMS). All prepared DESs were characterized in terms of their water content, viscosity, wettability and tribological properties. The friction coefficients were measured using steel spheres against Si surfaces. The most promissory DESs showed a good tribological performance, both in terms of friction and wear reduction comparing to commercial lubricants.

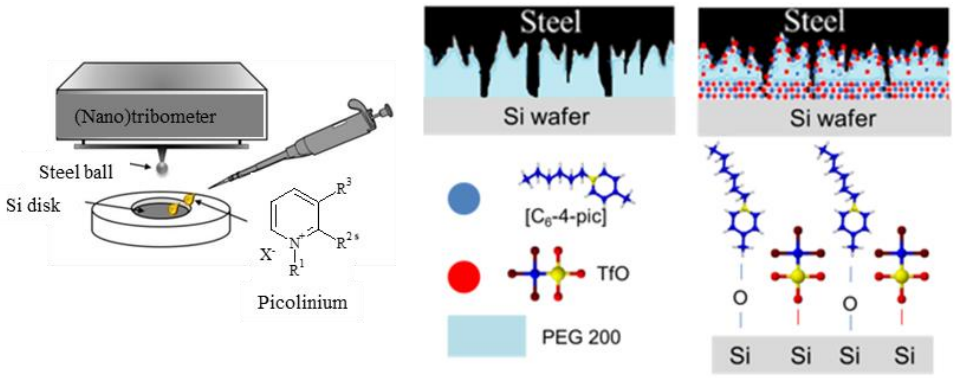

Figure 1. Schematic representation of the (nano)tribometer system and the interactions between the DESs and the Si surface.

Acknowledgements

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P53

Adsorption of ethane and ethylene by glycerin-based adsorbents

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Separation of light olefins from their paraffin counterparts is nowadays one of the key separation processes carried out in the chemical industry. Ethylene and propylene are two light olefins and for their applications as core building blocks of high-value products, they need to be separated from ethane and propane, respectively. These olefins are two large volume organic chemical feedstocks, being key components in the chemical and petroleum industry belonging to the backbone of the petrochemical industry[1,2]. In this work, we synthesize activated carbons for applications as ethane/ethylene adsorbent. Glycerin, a byproduct of biodiesel production, was used as precursor to synthesize new microporous glycerin-activated carbons and the resultant adsorbents were characterized by adsorption nitrogen at low temperature, FTIR, SEM, elemental analysis and pHPZC. Results showed that the glycerin-activated carbons present the highest surface area (1166-2150 m^2g^{-1}) and pore volume (0.63-1.03 cm^3g^{-1}). More interestingly, all the glycerin-activated carbons exhibited higher adsorption capacity of ethane over ethylene. Its C_2H_6 adsorption capacity was up to 8.92-14.81 mmol/g and its C_2H_6/C_2H_4 adsorption selectivity was in the range of 0.98-2.40. Therefore, a low-cost byproduct of biodiesel production – glycerin – can be transformed in a valuable material with promising properties for adsorption-separation of C_2H_6/C_2H_4.

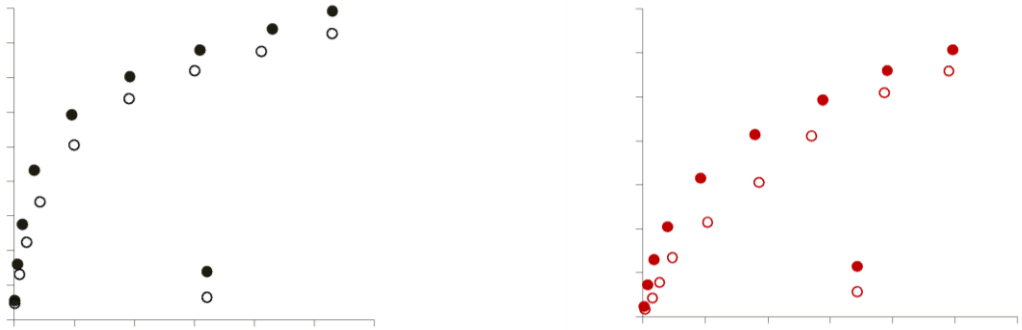

Figure 1. Adsorption isotherms of ethane and ethylene at 25 °C on mentioned samples.

Acknowledgements

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P54

Innovative analytical approaches to monitor forest volatile organic compounds (VOCs) in extreme fires perspective

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Climate change is drastically fostering higher levels of vegetation growth and fuel accumulation, which contributes to the ignition of extreme wildfires. As solid-phase microextraction (SPME) and bar adsorptive microextraction (BAμE) have been used for trace analysis of several classes of organic compounds, we proposed a comparative study of their performance in the headspace (HS) mode followed by gas chromatography coupled to mass spectrometry analysis for monitoring volatile organic compounds (VOCs) released from leaves of four tree species at different temperatures. The results obtained suggest that higher temperatures increase the VOCs emitted through the leaves, while HS-BAμE assays indicated that this approach might be a cost-effective alternative for their analysis. An assessment of the spatial distribution of leaves in the Portuguese forest using information from the vertical structure of the National Forest Inventory was analysed based on bulk density of canopies of the main forest tree species. This information, coupled with the percent cover by vertical strata, gave an estimate of the distribution of leaf biomass per species and per stratum. The coupling of this information with information on the VOCs release by unit biomass of leaves allow the estimation of the potential concentration of gases at the volume occupied and the area covered by the canopies. In addition, the Sentinel 5-P TROPOMI potential to monitor carbon monoxide (CO) before, during and after extreme fire events in Portugal was assessed. The spatial distribution and trends of CO column during the fire vent were evaluated and linked with the *in-situ* data. The Sentinel 5-P TROPOMI's CO data after consecutive digital processing steps showed the ability to follow fluctuations in CO concentrations. Moreover, significant differences were found when a quantification of the fire's influence on CO column concentrations (close vs away from the burning area) was performed through a spatio-temporal analysis.

Acknowledgements

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P55

Solution enthalpies of paracetamol in choline chloride-ethylene glycol eutectic mixtures

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Deep eutectic solvents are a novel class of solvents which have been studied extensively in recent years [1]. These solvents are formed mixing two (or more) components, which in certain compositions have a lower melting point when compared with the original constituents. Despite multiple characterizing efforts, thermodynamics studies namely solution enthalpies are still rare in this class of solvents.

In this work we report the solution enthalpies of paracetamol at 298.15 K in choline chloride-ethylene glycol eutectic mixtures using a semi-adiabatic isoperibol solution calorimeter (Figure 1), continuing previous studies with other solutes in conventional solvents [2].

Figure 1. Thermometric 2225 solution calorimeter

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P56

Optimization of the uncertainty in the measurement of variations of dissolved oxygen in environmental systems

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Dissolved oxygen concentration in water is a crucial parameter to assess the condition or evolution of aquatic ecosystem health. This determination can be performed using an electrochemical sensor or the reference Winkler method that allows a more reliable measurement of this parameter. The comparison of dissolved oxygen values determined on two occasions or two samples requires calculating the measurement uncertainty. This uncertainty is also relevant to understand if the determination has adequately low uncertainty.

This work describes the detailed assessment of dissolved oxygen determinations' performance aiming at the 'bottom-up' quantification and optimisation of the measurement uncertainty. The visual end-point detection's uncertainty was estimated by the difference between observed measurement precision and combined models of all precision components except the end-point detection [1-3]. A user-friendly MS-Excel spreadsheet that allows applying the developed uncertainty evaluation procedure was developed.

The determination of dissolved oxygen from analytical portions not lower than 50 mL is fit for environmental monitoring. It allows measurements between 0.3 mg L^{-1} and 14.6 mg L^{-1} with an expanded uncertainty between 0.36 mg L^{-1} and 0.74 mg L^{-1} for a 95% confidence level. This uncertainty allows differentiating dissolved oxygen values between 0.51 mg L^{-1} and 1.0 mg L^{-1} with less than a 5% probability of being wrongly assumed a relevant difference [1]. The described uncertainty evaluation strategy can also be used in other titrimetric determinations [1].

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P57

Atmospheric mercury concentrations and vegetation-air Hg0 fluxes in saltmarshes from Tagus estuary

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In situ air concentrations of gaseous elemental mercury (Hg^0) and vegetation-atmosphere fluxes were quantified in two saltmarshes of the Tagus estuary colonized by plant species *Halimione portulacoides* and *Sarcocornia fruticosa*. One saltmarsh (CN) presented high Hg-contamination due to a nearby chlor-alkali unit and the other (ALC), located in the Natural Reserve, had low-to-moderate Hg levels. Air Hg^0 concentrations were measured using a Tekran 2537A and the fluxes through a dynamic flux chamber.

Concentrations of Hg^0 were higher at CN (1.08–18.15 ng/m^3) than in ALC (1.18–3.53 ng/m^3) without statistical differences between plants from each site. While air Hg^0 concentrations at ALC varied diurnally and were positively correlated with meteorological parameters, the highest air Hg^0 concentrations at CN were found during the night-time. These results suggest that photoreduction was not driving the air Hg^0 concentrations at CN. Vegetation-air Hg^0 fluxes were low in ALC and ranged from -0.76 to 1.52 ng/m^2 (leaf area)/h for both plants. Higher Hg fluxes were observed for both plants in CN, ranging from -9.90 to 15.45 ng/m^2 (leaf area)/h. Here, the mercury fluxes were considered less reliable due to large and fast variation of ambient air Hg^0 concentrations, which may have been influenced by emissions from the nearby chlor-alkali plant and/or the known historical contamination. Additionally, the lower height of planetary boundary layer might also have influenced the ambient air Hg^0 measurements and consequently the calculation of vegetation-air Hg^0 fluxes. Nevertheless, diel variation of land and sea breezes may have an effect on the regional distribution of atmospheric Hg^0.

Further investigation is required concerning the improvement of the experimental setup to verify and monitor local sources of atmospheric Hg^0 emissions, and evaluate vegetation-air Hg^0 fluxes, especially in heavily contaminated sites. Future work should investigate similar Hg "hotspots" with seasonal variations and with different saltmarsh plant species.

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P58

Application of bar adsorptive microextraction for the determination of tricyclic antidepressants in urine samples

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Tricyclic antidepressants (TCAs) are widely involved in clinical and forensic cases, given the TCAs narrow therapeutic/toxic index. Thus, the determination in biological matrices is necessary for emergency toxicological screening, drug abuse testing, forensic medical examinations for probable fatality caused through overdose, for monitor therapy and for pharmacokinetic studies [1,2].

We propose an analytical methodology for the determination, in biological matrices, of amitriptyline, mianserin, trimipramine, imipramine, mirtazapine, and dothiepin, 6 common TCAs. The enrichment process was performed using bar adsorptive microextraction (BAμE) followed by micro liquid desorption, in combination with large volume injection-gas chromatography–mass spectrometry operating in the selected-ion monitoring acquisition mode (BAμE-LD/LVI-GC-MS).

Under optimized experimental conditions, the detection limits achieved for the six TCAs ranged from 0.2 to 1.6 μg L-1 and we obtained suitable linearity (r2 > 0.9960) between 10.0 and 1,000.0 μg L-1. The developed analytical methodology provided unsignificant matrix effects (90.2-112.9 %, RSD ≤ 13.9 %), high recovery yields (92.3-111.5 %, RSD ≤ 12.3 %) and a remarkable overall process efficiency (ranging from 84.9 % to 124.3 %, RSD ≤ 13.9 %). The developed and validated methodology was successfully applied for screening the six TCAs in real urine matrices.

The proposed analytical methodology proved to be an eco-user-friendly approach to monitor trace levels of TCAs in complex urine matrices and an outstanding analytical alternative in comparison with other microextraction-based techniques

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P59

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.

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Acknowledgements

This work was supported by Fundação para a Ciência e Tecnologia, Projects UIDB/00100/2020 and UIDP/00100/2020.

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P60

Bottom-up evaluation of the uncertainty of quadratic calibrations: Determination of mercury in marine sediments by direct atomic spectroscopy

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The objective interpretation of an analytical result is only possible if it is known the respective uncertainty that expresses the impact of random and systematic effects on the measurement[1]. The evaluated uncertainty is also relevant to assess if measurement is performed with adequately low uncertainty[2]. The detailed bottom-up evaluation of the measurement uncertainty also allows identifying and optimising the most relevant uncertainty component[3,4].

The evaluated measurement uncertainty depends on the analytical performance, the uncertainty of the values of used references or standards, and the quality of measurement modelling. Some laboratories invest in the detailed modelling of their performance to produce reference materials with adequately low uncertainty to support routine analysis.

In their role as Designated Metrology Institute, the Hydrographic Institute develops their measurement capabilities to produce the highest quality reference measurements to support the comparability of lower metrological level measurement. This goal requires the detailed modelling of the performance of used analytical operations and instruments.

Some analytical instruments have a response proportional to the measured quality, while others show a curvilinear signal. The signal curvature can be adjusted to a quadratic model, but the regression process is affected by signal precision values and variation, and calibrator values uncertainty. The modelling of these calibrations is hampered by the correlation between calibrators values and estimated regression parameters. No tools have been developed so far for the detailed validation and evaluation of complex curvilinear calibrations.

This work describes the development of a computational tool based on Monte Carlo Simulations and alternative regression models for the bottom-up assessment of the uncertainty of total mercury measurement in marine sediments by Direct Atomic Spectrometry (Direct Mercury Analyzer, DMA-80 Tricell). The produced measurements should be associated with a measurement uncertainty at least one fourth smaller than the required for environmental monitoring to be used in reference materials production for this analytical work.

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P61

Unified pH scale method for industrial applications - an interlaboratory comparison

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pH= - lg a_{H+}, a well-established concept for the acidity of aqueous solutions, is one of the most important measured parameters in science and industry, playing an important role in environmental studies, health, food, textiles and material reprocessing.

Over the last century, the comparison of pH between different media hasn't been possible due to theoretical and practical constraints which led to several incompatible pH scales. In 2010 the concept of a unified acidity scale common to all systems, namely different solvents, reporting to a reference state where the chemical potential of H^+ equals zero, was conceived, defining an absolute value, pHabs, which overcame this issue [1].

Based on differential potentiometry against anchor solvent, water, H_2O, Project UnipHied aims to establish a reliable and universally applicable procedure for measuring $p\mathrm{H}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of any system and to develop a validated set of calibration standards for a wide variety of media [2].

In order to contribute to this purpose an interlaboratory comparison was performed at the 10 participating institutes involved in the project. Addressing the different challenges related to $p\mathrm{H}_{\mathrm{abs}}^{\mathrm{H_2O}}$ measurements, procedures were evaluated in three samples of different complexity:

- aqueous complex solution approaching seawater: equimolal TRIS (0.04 m) - $TRIS.H^+$ (0.04 m) buffer solution prepared in a high ionic strength (~ 0.4 m) NaCl solution;
- water-ethanol mixture: equimolal phosphate (0.015 m Na_2HPO_4: 0.015 m KH_2PO_4) prepared in the water-ethanol mixture containing 50 wt% of ethanol;
- pure ethanol: a formate buffer (10 mM).

Through the participation in this interlaboratory comparison, our laboratory demonstrated the ability to measure $p\mathrm{H}_{\mathrm{abs}}^{\mathrm{H_2O}}$ of samples with different complexities. The comparison has provided consistent results, validating the developed method which can be considered suitable for measurements in industrial applications, namely those dealing with liquid chromatography [3].

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P62

CO_2 methanation as an alternative for decarbonising cement sector: The impact of oxygen in the feed

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The environmental concerns regarding the expansion of renewable sources for electricity production are partially related with its intermittency. Therefore, valorising the excess of renewable electricity through the production of green H_2, from water electrolysis, constitutes a promising alternative. Furthermore, CO_2 from sectors with high emissions contribution can be successfully converted into synthetic natural gas, by using renewable H_2. Overall, this strategy can be considered a potential alternative for cement industries decarbonisation.

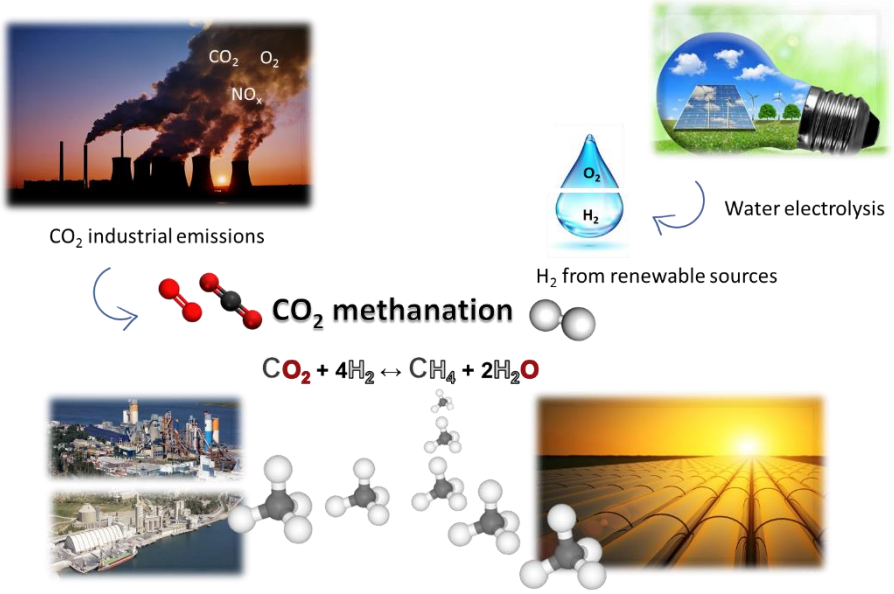

Figure 1. Power to Gas concept.

CO_2 methanation requires the use of catalysts due to the stability of carbon dioxide molecules. Thus, 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 etc. have been widely analysed in the literature. Among them, the utilization of zeolite-based catalysts has been gaining attention, mainly due to their easily tunable properties. Nevertheless, the industrial implementation of CO_2 methanation requires evaluating the effects of impurities present in real effluents in the properties and performances of the catalysts. In the cement context, studying the influence of O_2 in the reaction feed is mandatory, as it is reported as one of the deactivation causes, mainly due to metals reoxidation or consumption of the H_2 based on the oxygen hydrogen reaction.

Consequently, in the present work, three materials (Ni/Zeolite, Ru/Zeolite and a Commercial methanation catalyst) were used as catalysts for CO_2 methanation. Several characterization techniques were used (XRD, TGA, H_2-TPR, N_2 adsorption) and conventional (1 bar and 250-450 ºC) and cyclic CO_2 adsorption/hydrogenation tests (with and without O_2 in the feed) were performed.

Results indicated that the nature of the active metal influences the resistance towards the presence of O_2, even if the catalytic performances under conventional tests were similar. In this way, Ru exhibited a higher resistance towards reoxidation, in accordance with literature, while the commercial sample presented the highest deactivation.

Acknowledgements
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P63

Flexible and reliable identification strategy of microplastics by micro-ATR-FTIR

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Worldwide plastic production exceeds 368 million tons, and over 62% of marine litter is plastic now[1,2]. Microplastics are plastic pieces ranging from 1 µm to 5 mm. The threat of microplastics to small organisms and consequently to the entire food chain, including humans, attracted the scientific community to the monitorization of microplastics in different compartments and matrices. However, the impact of microplastics is only possible to understand if this contamination is characterized adequately and objectively regarding the physical and chemical properties (*i.e.*, polymer type) of particles. The polymer type is commonly identified by Fourier-Transformed-Infrared spectroscopy, FTIR, where the acquired infrared spectrum works as a molecular fingerprint of the plastic. Identifying microplastics from the infrared spectrum can be challenging in some cases, particularly when a biofilm covers the particles or whenever spectral inconsistencies appear due to differences in plastic additives and copolymers, ageing, or other coating types.

This work describes the development and validation of a methodology towards the automatic identification of microplastics by micro-ATR-FTIR, overcoming the complexity and time consuming of a manual interpretation of characteristic spectral bands. The automatic identification of the IR spectra was supported on a fast mathematical comparison between the unknown microparticle and reference spectra using different signal transformations, match algorithms and thresholds. A two stages strategy allowed to distinguish the most similar polymers from a narrow IR spectral range. The performed identifications are associated with a true positive rate, *TP*, and a false positive rate, *FP*, not lower or greater than 95% and 5%, respectively. The methodology for identifying microplastics with adequate uncertainty was successfully applied to the identification of Polyethylene, PE, Polyethylene terephthalate, PET, Polypropylene, PP, and Polystyrene, PS, microparticles from sediments collected in Portuguese rivers, improving the preliminary results on the polymer type identification already reported[3,4].

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P64

Qualitative determination of stimulants by GC-MS under the world anti-doping agency analytical requirements

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The World Anti-Doping Agency's (WADA) mission is to lead a collaborative worldwide movement for doping-free sport. WADA has established a list of prohibited substances (International Standard - Prohibited List 2021), in which stimulants are one of its main subgroups. This class consists of about 70 chemical substances with different physical-chemical properties, often promoting great challenges from an analytical point of view. Even so, any proposed analytical methodology must be developed in compliance with the WADA requirements, present in specific technical documents (TD2019MRPL, TD2021IDCR) and suitable for most of the stimulants present in that list, as well as with ISO 17025 [1].

State-of-the art analytical methodologies to monitor stimulants in urine samples at the trace level, used to be based on the application of solid phase extraction followed derivatization prior to analysis by gas chromatography coupled to mass spectrometry [2].

In the present work, we discuss the validation steps of an analytical methodology developed and dedicated to monitor stimulants like amphetamine, cocaine, benzylpiperazine and propylhexedrine in urine matrices. Parameters such as selectivity/specificity, identification criteria, limits of identification, recovery, carryover, robustness and stability, as well as accuracy through proficiency tests, were evaluated in order to check if the methodology is fit-for-purpose in compliance with the official technical documents.

Furthermore, to give a step-up into the modern microextraction techniques, additional assays were performed through bar adsorptive microextraction (BAμE), which have shown to be eco-friendly, easy to prepare and with remarkable cost-benefits in sample preparation. The results obtained by BAμE demonstrated good performance and an alternative approach, to monitor stimulants-controlled drugs inside the sports context [3, 4].

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P65

New silver(I)-tazobactam coordination frameworks synthesized by mechanochemistry: a strategy to improve drugs

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The application of metal-organic frameworks in drug discovery has been increasing, mainly for controlled drug delivery and release. These pharmacological applications are very promising and have as a requirement a biosafety character, which must be ensured through a careful selection of the organic linker and the metal cation [1]. The design of such architectures using antibiotics directly as organic linkers has been studied by our group, giving rise to new antibiotic coordination frameworks (ACFs) with promising results [2]: significant changes in the solubility, and increased antibacterial efficacy.

In this work, we present new Ag(I)-ACFs with tazobactam (Figure 1) acting as the linker. Tazobactam is a penicillinate sulfone effective against many susceptible organisms expressing β-lactamases [3]. The new frameworks can be envisaged as an alternative to improve the antimicrobial activity of the antibiotic making use of the synergistic effect of the metal. The main synthetic technique used was mechanochemistry, a promising pathway for green, sustainable, and safe chemistry [4].

Figure 1. Scheme of the synthesis of new Ag(I)-ACFs with tazobactam by ball milling.

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P66

Water solubility in (alkane + perfluoroalkane) mixtures and in perfluoroalkyl-alkanes: experimental and modeling with the SAFT-*γ* Mie GC approach

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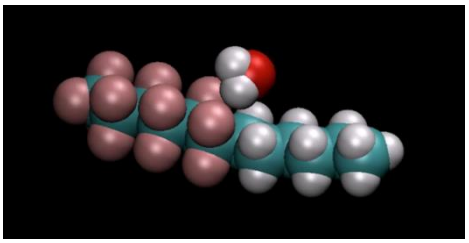
The solubility of water in liquid *n*-hexane, *n*-perfluorohexane and in their equimolar mixture was experimentally determined as a function of temperature. The solubility of water in the mixture is significantly higher than the average of the solubilities in the pure solvents, which lead to the suggestion, for the first time, that mixing hydrogenated and perfluorinated chains enhances the solubility of water in such systems.

A SAFT-γ Mie group-contribution approach that describes the phase behavior of *n*-alkanes, *n*-perfluoroalkanes, water and their binary combinations is used to calculate the solubility of water in the *n*-hexane + *n*-perfluorohexane mixture. This theoretical approach is used here to assess quantitatively how much the large deviations from ideality in the solvent mixture contribute to the water solubility behavior. The importance of a correct modelling of the non-ideality of the solvent mixture[1] is demonstrated by the quantitative prediction of the ternary behavior.

In addition, the same SAFT-γ Mie EoS is used to represent the solubility of water in a number of *n*-perfluoroalkylalkanes as a function of temperature, covering a range of relative lengths of the hydrogenated and perfluorinated chains. The theory can be used to correctly predict the relative extent of the solubility of water in the different solvents, in good agreement with experimental data. This is accomplished by using a single parameter to describe the strong attractive interaction between water and the CH_2CF_2 group at the junction between the hydrogenated and perfluorinated segments, which is known to be responsible for the increased solubility of water in these substances.[2]



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P67

Unveiling the industrial contamination and biogeochemistry of Platinum group elements in the Tagus estuary

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Platinum-group elements (PGE) raise concern due to their steady increase in the environment. Despite their low crustal abundance (<0.5 ng/g), PGE are extensively used in various technology-based sectors, including automotive, industry and health. Adequate assessment of PGE environmental risks is still missing and their biogeochemistry in aquatic ecosystems remains poorly understood [1]. Aligned with the UN 2030 Agenda, BIOGEOTECH and Tech-BIIAS are two challenging interdisciplinary projects that combine oriented fieldwork and novel laboratory experiments, aiming the upgrade and implementation of analytical procedures for PGE-Re determination in several matrices; evaluation of abiotic and biotic factors governing PGE biogeochemistry; and investigation of PGE cycling and fate in coastal systems. Both projects comply with CQE strategy being integrated into SUSChem thematic line, and their outcomes may be relevant for the other groups promoting inter-cooperation.

We hypothesized a PGE signature could be imprinted in sediments of the Tagus estuary, owing to industrial activities before the introduction of automotive catalytic converters. This study used sediment cores from two distinct industrial areas (BRR and CN) and a reference site (VF) in the estuary. Acid-digested samples were analysed for Pt and Rh by AdCSV, and for Pd by ICP-MS. At BRR, Pt showed the highest levels at 6-cm depth (17 ng/g) and all PGE incremented in 10–15-cm layer, depicting the historical ore processing and metals extraction during 1960/70s. PGE continuous input at CN, with Pd displaying the highest levels (6 ng/g) at surface, had a source in the nearby industry. The reference site VF mimicked CN down-core distribution likely due to tidal spreading within the estuary. Moreover, geochemical processes favoured PGE retention in sediments. Fractionation of PGE in sediments remains a challenging task due to analytical limitations. Despite that, this work contributes significantly to the current knowledge of PGE with industrial source emissions.

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P68

Mechanosynthesis of pyrazinamide coordination frameworks to improve antitubercular therapy

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The current antitubercular chemotherapy includes pyrazinamide, a well-known antimycobacterial agent applied in the treatment of tuberculosis. One of the major concerns of this treatment is its duration of 6 months, which can permit the emergence of drug resistant microorganisms and have a high impact in the burden for both patients and clinics. More efficient drug forms could contribute to reduce the length of the treatment, and limit this threat.

Our approach consists on the design of metal-organic frameworks enclosing antibiotics as ligands to produce antibiotic coordination frameworks (ACFs), aiming to improve the properties and antimicrobial activity of the starting antibiotics [1,2].

The privileged synthetic technique in our studies is mechanochemistry. This is a sustainable solid state environment-friendly technique that allows selective, efficient and fast reactions avoiding the use of solvents or using minimal amounts of solvents [3].

Here we present and characterize one novel hydrogen bonding manganese framework (I) and three new compounds with silver. Two of the new silver-based frameworks (II and III) presented enhanced antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus* and *Mycobacterium smegmatis* when compared with the free antibiotic (Figure 1) [4].

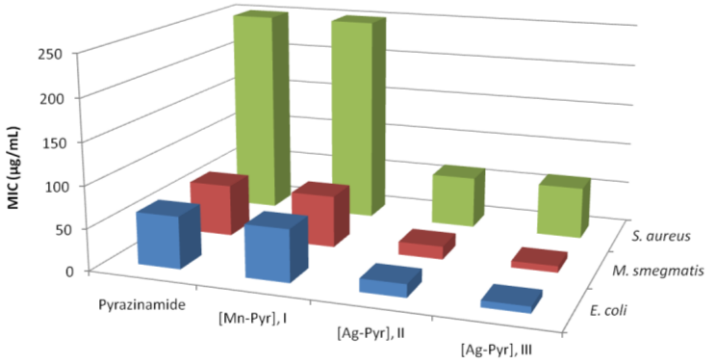

Figure 1. Minimal inhibitory concentration of the new antibiotic coordination frameworks.

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Supercritical fluids for microalgae biorefineries

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The decrease in the resources of fossil fuels, together with the global warming alarms, has led to an intensified search for alternative fuels.

Microalgae are nowadays an important subject of research as an energy source with applications for biodiesel, ethanol, methanol, methane and hydrogen. The use of microalgae biomass can be a promising alternative feedstock for next generation biofuels, since microalgae have a fast growth rate, by naturally fixing atmospheric CO_2 via photosynthesis; allow the use of non-arable land and non-potable water; its production is not seasonal; can be harvested daily; avoid environmental impacts [1]. On the other hand, microalgae biomass present an enormous potential ranging from biofuels, biochems and bioplastics to high-value compounds useful in the nutritional, cosmetic and pharmaceutical/medical industries [2]. However, at the moment, biodiesel derived from microalgae is still economically unsustainable, because its production costs are high [1,3]. Thus, the development of sustainable extraction processes of its high-value compounds is mandatory.

Supercritical fluid extraction (SFE) of bioproducts from microalgae has some advantages over the conventional solvent extraction methods, because the compounds can be obtained without contamination by the organic solvent and thermal degradation. Also, it is possible high efficiency of the extraction and the selectivity for certain compounds is more easily achieved with SFE than with organic solvent extraction. Moreover, SC CO_2 has also the advantage of using a non-toxic, non-flammable and cheap solvent.

SFE studies of high added-value compounds from microalgae such as *Dunaliella salina*, *Chlorella vulgaris*, *Haematococcus pluvialis* and *Nannochloropsis* sp have been carried out [4-6]. The effect of several SFE experimental parameters (temperature, pressure, co-solvent, biomass pre-treatments) on the yield and selectivity of extraction, as well as fractionation of the extracts, was evaluated.

The most important results achieved during the SFE of bioactive compounds from these microalgae will be presented and discussed.

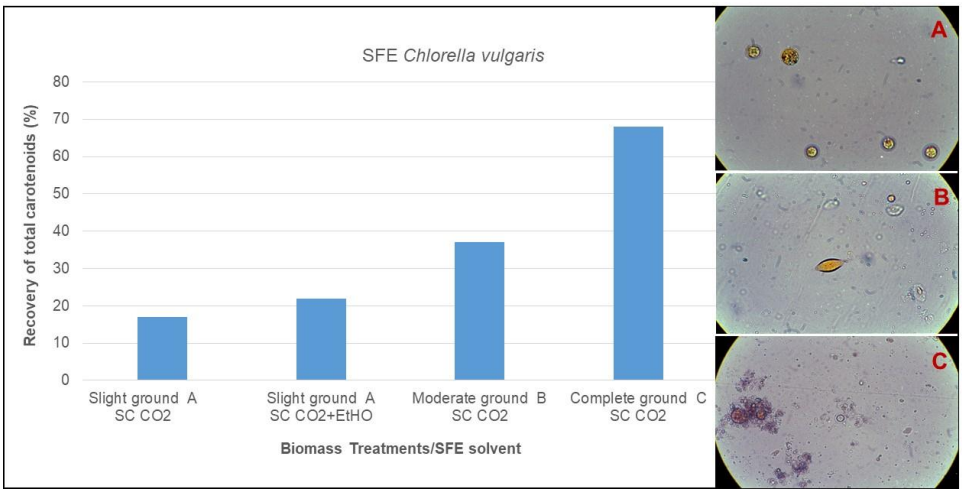

Figure 1. Recovery of carotenoids from microalgae *Chlorella vulgaris*: several degrees of crushing and SC solvents

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P70

Valorization of sugars and derivatives obtained by catalytic depolymerization of lignocellulosic materials for the production of sustainable polymers

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Biomass of lignocellulosic origin has been preferentially used for the production of bio-oil by liquefaction due to its abundance and easy access [1,2], in addition to allowing the obtaining of green chemical products and / or the conversion into sustainable energy sources. [3]. Through the liquefaction process, hemicellulose and cellulose lead to the formation of sugars whose composition has not yet been investigated in depth [4]. In this context, the study of the lignification 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 in view of the state of the art. [5]. Levulinic acid has been identified as a promising molecule with regard to sustainable chemical products, and can be produced from renewable resources such as lignocellulosic biomass [6]. Angelolactone can be produced from levulinic acid through an intramolecular condensation process followed by dehydration [7], presenting itself as an important raw material in the synthesis of new sustainable polymers [8]. 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-industrial. The valorization of sugars is still a low cost alternative for the polymer and construction industry (cement industry), as well as for the agro-industry. The relevance of this work is also due to the lack of in-depth studies that lead to the elucidation of mixtures resulting from liquefaction, as well as the structure of the products originated and their applications.

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P71

Development of amide functionalized metal organic frameworks for cascade reactions: a comparative study

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Metal–organic frameworks (MOFs) 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 heterogeneous catalysts, magnetism, nonlinear optics, gas storage and separation, etc[2]. Moreover, MOFs constructed from amide-based linkers have attracted considerable attention due to their interesting topologies as well as catalytic properties[3]. Thus, we have synthesized various amide functionalized multifunctional carboxylate ligands and employed them for the construction of MOFs having different dimensionality. We have characterized our synthesized MOFs by X-ray single crystal diffraction, elemental microanalysis, IR spectroscopy, thermogravimetric analysis and powder X-ray diffraction analysis. These MOFs heterogeneously catalysed the cascade deacetalization−Knoevenagel condensation reactions under conventional heating, microwave irradiation or ultrasonic irradiation (Figure 1). Comparative studies show that ultrasonic irradiation provides the most favourable method. Moreover, the catalysts can be reused at least for five consecutive cycles without losing activity significantly.

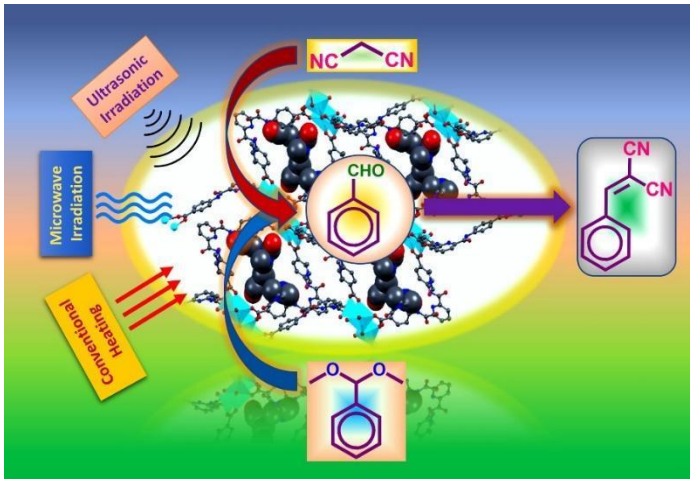

Figure 1. One-pot tandem deacetalization-Knoevenagel reactions catalyzed MOF using conventional heating, microwave and ultrasonic methods.

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P72

Vanadium Complexes in Oxidation Catalysis

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Oxidovanadium complexes in high-oxidation states are active catalysts towards various oxidative organic transformations [1,2]. They have been widely used as homogeneous or heterogeneous (supported) catalysts in several oxidation processes of industrial interest in the presence of a suitable oxidant e.g., alkyl hydroperoxides, H_2O_2 or O_2, under mild conditions. The feasibility of high valent vanadium complexes in oxidation catalysis is govern by (a) the easily interconvertible vanadium oxidation states (where +4 and +5 are the most stable ones under aerobic conditions), (b) they can form various possible coordination numbers, (c) the high affinity of the vanadium towards oxygen and (d) the Lewis acid character of the vanadium centers. Oxidovanadium complexes onto a solid support have the advantage of catalytic recycling.

In this presentation, the catalytic activity of various oxidovanadium complexes under homogeneous and supported heterogeneous catalysis towards selective oxidation reactions, such as alkanes and alcohols oxidation etc. will be discussed [1,2].

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P73

A novel tetrazole-saccharinate Zn(II) catalyst acting on selective oxidation of benzyl alcohols; The role of the ligand and the reaction mechanism

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The use of zinc catalysts, particularly on oxidation reactions comprising different functional groups present in relevant small organic molecules, although less frequent when compared to copper or iron catalysts is growing significantly with good results. Evidence of this is the research work offered here!

In this presentation, we open a facile and selective transformation of a series of benzyl alcohols to the corresponding aldehydes promoted by a novel tetrazole-saccharinate Zn(II) catalyst.[1] The reaction, activated by microwave radiation, proceeds typically in a few minutes under effective smooth conditions by using TBHP (70%. aq.) as oxidizing agent, in absence of any organic solvent and conveys some functional group tolerance. Experimental observations allude to a radical reaction mechanism comprising oxygen- and carbon-centered radicals.

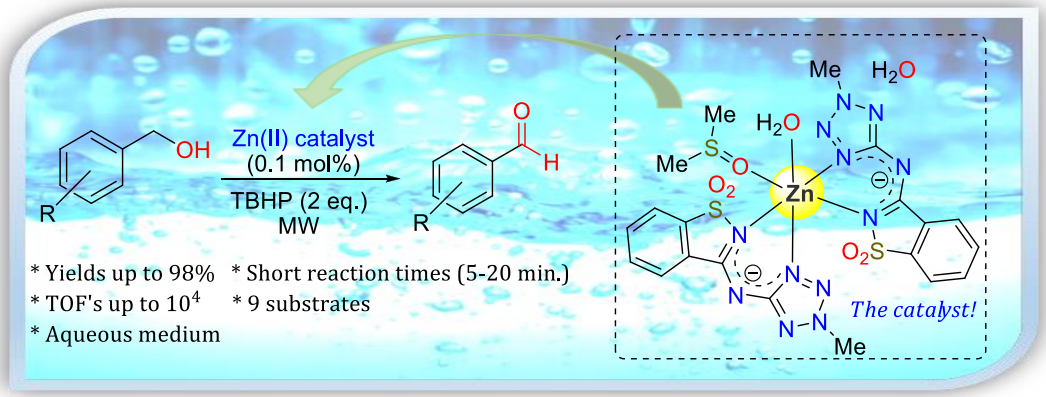

Figure 1. Overview of the microwave-assisted oxidation of benzyl alcohols promoted by a novel tetrazole-saccharinate Zn(II) complex.

Acknowledgements

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P74

Application of the modified KAT model equation to quantify solute-solvent interactions in tertiary alkyl halides heterolyses

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A few years ago we showed that the application of the Kamlet-Abraham-Taft (KAT) model equation provided robust and predictive quantifications of the main solute-solvent interactions which prevail in the heterolysis reactions of three tertiary alkyl halides with different structural characteristics – Fig. 1 [1]. However, a subsequent publication from another research group has tested other sets of model equations and concluded that disjointed results were found for one of our substrates due to an alleged insufficient diversity of solvents [2].

Very recently, we have successfully devised a modified version of the original KAT model equation, that separates the solvent's polarizability and dipolarity terms [3]. In the present work we test and compare the ability of the developed, modified, model to quantify solvent effects against other well-known equations in the same set of solvents, previously subjected to criticism. The *a priori* exclusion of the corresponding hydrogen bond acceptance (HBA) basicity descriptor for all tested models allowed us to obtain similar responses in all cases, thus providing a solid answer to Laurence's et al. comments. *En route*, the overall better performance of the modified KAT model was also observed.

The attained results provide a further rational regarding the stabilization of the transition states of these solvolyses by nucleophilic solvents, a subject that we have addressed in a recent paper [4].

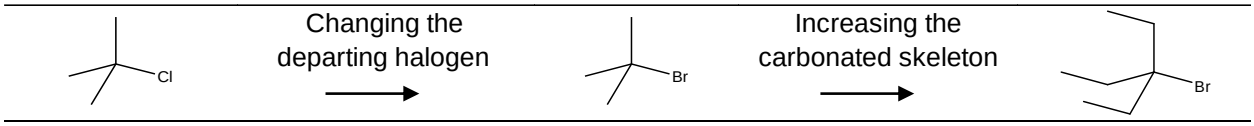

Figure 1. Studied tertiary alkyl halides and respective structural differences.

Acknowledgements

The authors acknowledge support from Fundação para a Ciência e a Tecnologia, Portugal (UIDB/00100/2020). This communication is dedicated to the memory of Professor Michael H. Abraham.

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P75

New iminopyrrolyl titanium hydroamination catalysts

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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 in this communication the synthesis of a family of sterically congested and electronically unsaturated mono(5-aryl-2-iminopyrrolyl)titanium(IV) complexes.

This set of five-coordinate Ti(IV) compounds were prepared in very good to excellent yields by treatment of the 5-R-2-[*N*-(2,6-diisopropylphenyl)formimino]-1*H*-pyrrole (R = 2,6-Me_2-C_6H_3 (**1a**), 2,4,6-*i*Pr_3-C_6H_2 (**1b**), 3,5-$(CF_3)_2$-C_6H_3 (**1c**) and CPh_3 (**1d**) with tetrakis(dimethylamido)titanium(IV). The resulting amido complexes [Ti(L)$(NMe_2)_3$] were tested in the cyclohydroamination of terminal olefins, most of them revealing to be effective precatalysts for this transformation (Figure 1).

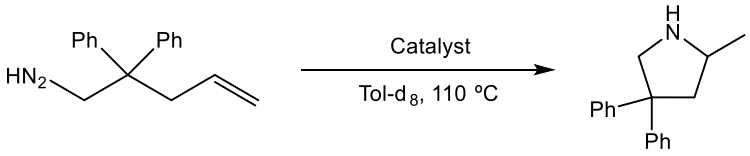

Figure 1. Catalytic reaction of cyclohydroamination.

Additionally, in order to study the effects of the replacement of the amido ancillary ligands on the hydroamination reactivity, two other precatalyst were prepared. Reaction between the 5-pyrrolyl substituted titanium trisamido complex [Ti{κ²*N,N'*-5-(2,6-Me_2-C_6H_3)-NC_4H_2-2-C(H)=N(2,6-*i*Pr_2-C_6H_3)}$(NMe_2)_3$] with an excess of trimethylsilyl chloride in the presence of pyridine afforded the corresponding complex [Ti(L)$Cl_2(NMe_2)Py_2$] in good yields.

Furthermore, the reaction between a newly synthesised *N*-silylated pyrrole derivative [5-(2,6-Me_2-C_6H_3)-$Me_3SiNC_4H_2$-2-C(H)=N(2,6-*i*Pr_2-C_6H_3)] with [$TiCl_4$] easily afforded the respective Ti(IV) complex [Ti(L)Cl_3] in very good yields, confirming this *N*-silylated compound as a good ligand transfer reagent. Conversely to the amido complexes, these precatalysts revealed no catalytic activity towards cyclohydroamination.

Acknowledgements
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P76

Hydrosilylative reduction of aldehydes and ketones catalysed by a 2-iminopyrrolyl manganese(II) catalyst

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The reduction of carbonyl groups is present in the synthesis of many commodity chemicals [1]. Metal-catalysed hydrosilylation has become an important alternative for such reactions, owing to the stability and versatility of organosilicon compounds, particularly with the advent of noble metal-based catalyst systems. However, to maximize the sustainability of those catalytic processes, there has been a clear 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 catalysing the atom-economical hydrosilylative reduction of aldehydes and ketones to the respective alcohols (Figure 1). Utilizing very mild conditions, a maximum turnover frequency of 5700 h^{-1} was obtained, via a silyl-Mn(II) mechanistic route, as asserted by experimental and theoretical efforts.

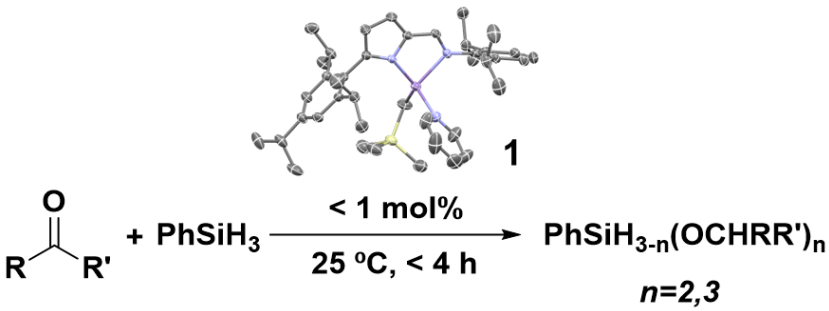

Figure 1 Hydrosilylative reduction of aldehydes and ketones catalysed by **1**.

Acknowledgements
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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P77

Using Cu(II) cyclam-based complexes to unveil antibacterial activity

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Cyclam is a tetraazamacrocycle with several applications in diverse fields of medicine[1]. In particular, bis-cyclam derivatives were found to be highly active and selective HIV inhibitors against both HIV-1 and HIV-2 strains by interaction with the CXCR4 receptor[2]. More recently, cyclam derivatives and their metal complexes revealed anticancer[3-4], antimalarial[5], and antischistosomal[6] and antimicrobial[7-9] properties. The *trans*-disubstituted cyclam salt $[H_4\{H_2(^{4\text{-}CF3}PhCH_2)_2Cyclam\}]Cl_4$ was described as the most active compound against the Gram-negative *Escherichia coli* and the Gram-positive *Staphylococcus aureus* bacteria[8]. However, the molecular interactions between cyclams and bacteria remains unknown until now.

The Cu(II) cyclam-based complex $[\{H_2(^{4\text{-}CF3}PhCH_2)_2Cyclam\}Cu(H_2O)_2](CH_3COO)_2$ was synthesized, characterized and used to gain insights on the mechanisms of action against bacteria. Results on its activity and cellular compartmentalization in *E. coli* cells (Figure 1) will be presented and discussed.

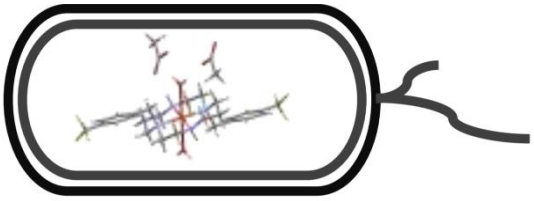

Figure 1

Acknowledgements

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P78

Nanostructured Co-oxide for the reduction of nitroarenes

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Aromatic amines are important intermediates in the synthesis of chemicals such as antioxidants, dyes, pigments, pharmaceutical and agricultural materials [1]. These compounds can be accessed by the reduction of nitroarenes using reducing metals such as zinc, tin or iron in the presence of an acid or salts [2,3]. An issue for the application of catalysts for nitro reduction is selectivity, easy recovery and recycling of the catalysts, properties that assist solely heterogeneous catalysts being advantageous over their homogeneous counterparts. Research in this field is very active to take advantage of the high surface area, easy separation and reusability of heterogeneous catalysts ranging from metal nanoparticles to bulk materials [1]. Cobalt oxide nanomaterials have been known as promising catalysts for use in the reduction of nitroaromatic compounds [4]. Various methods are available to prepare oxide-based catalysts – solid-state reaction, precipitation, sol-gel or hydrothermal – with a final calcination step at a high temperature of the raw materials that are preliminarily prepared by those methods. These protocols allow tuning the surface properties to prepare promising metal oxide catalysts, obtained after the final calcination step.

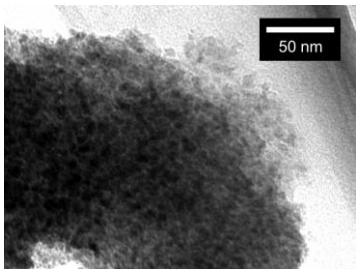

Figure 1. TEM image of Co oxide-based nanomaterial

In this work nanosized Co oxide-based catalysts were prepared at three different temperatures of calcination and under two different atmospheres (N_2 and air).

The structure and surface of the nanosized Co oxide-based materials was characterized by powder X-Ray Diffraction (pXRD), Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM). To study performance of these new Co oxide-based nanomaterials the reduction of different nitroarenes was carried out (p-nitrophenol, p-nitroanisole, m-nitrophenol, p-nitrotoluene, 1-chloro-p-nitrobenzene, p-nitroaniline and methyl-p-nitrobenzoate) using sodium borohydride (NaBH4) as reducing agent.

Results showed that the Co oxide nanomaterials led to 100% conversion and selectivity after 5 min across the tested substrates. The efficiency of the catalysts showed a higher catalytic effect for the calcined ones under N_2 atmosphere at 250 ºC.

Acknowledgements

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P79

Cork-derived activated carbon as a support for CO_2 methanation catalysts

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CO_2 methanation is a key catalytic reaction that can contribute to carbon dioxide emissions abatement and allows storing the temporary surplus of renewable electricity in the natural gas grid (Power-to-Gas). Supported catalysts containing transition (Ni, Co, Fe) and noble (Ru, Rh) metals have been applied in this reaction [1]. Among them, the catalytic systems containing Ni are the most promising due to their high catalytic activity, methane selectivity and economic viability. In terms of supports, Al_2O_3, SiO_2, CeO_2, ZrO_2, hydrotalcites, carbons or zeolites have been reported, being concluded that its nature has a significant impact on catalysts' properties and performances [1].

The use of activated carbon (AC) as support for CO_2 methanation catalysts has not been widely studied in the literature yet, but promising results were reported so far [1,2]. Indeed, it was suggested that the high surface area of AC allows storing high quantities of both H_2 and CO_2, turning Ni/AC into an active catalyst for this reaction. Furthermore, the use of waste materials as AC precursors constitutes an interesting strategy which deserves more studies [1].

Consequently, in this work cork waste was used as AC precursor for the synthesis of Ni and Ni-Ce catalysts towards CO_2 methanation. AC was prepared by physical activation [3] and metals were incorporated by incipient wetness impregnation. Samples were characterized by N_2 adsorption, CO_2 adsorption, XRD and TGA, being finally tested under CO_2 methanation conditions (1 bar, 86100 ml h^{-1} g^{-1}, P_{CO2} = 0.16 bar). Among all, the synthesized AC presented high textural properties (Figure 1) and the bimetallic catalyst presented the smallest Ni^0 crystallites size. The prepared samples exhibited promising results, confirming the interest of cork waste utilization as a support precursor.

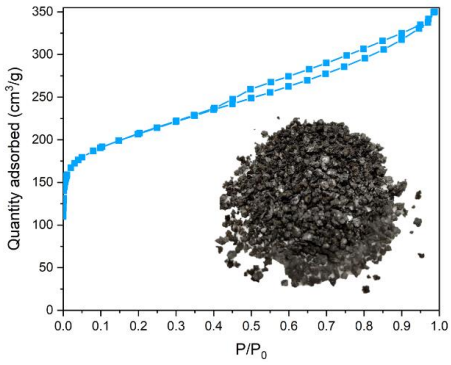

Figure 1. Isotherm of the AC synthesized in this work.

Acknowledgements
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P80

CO_2 methanation: A powerful strategy for biogas upgrading

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Biomethane is a flexible energy vector which can be used as vehicle's fuel, electricity source and even in heating [1]. Consequently, it can efficiently contribute to the reduction of greenhouse gases emissions typically associated to these sectors. Biomethane can be obtained from the cleaning and upgrading of biogas, produced by the anaerobic fermentation of organic waste and containing 30-60 wt% CO_2 and 40-70 wt% CH_4.

As shown in Figure 1, biogas upgrading to biomethane requires CO_2 removal, being this step carried out through adsorption, absorption or even membrane processes [2]. However, an alternative strategy which leads to a more efficient valorisation of biogas is the direct catalytic conversion of the CO_2 into methane (CO_2 methanation) using green H_2 produced from renewable electric energy (Power-to-Gas). This alternative maximizes the valorisation of the renewable carbon coming from biomass digestion and increases the yield in green natural gas.

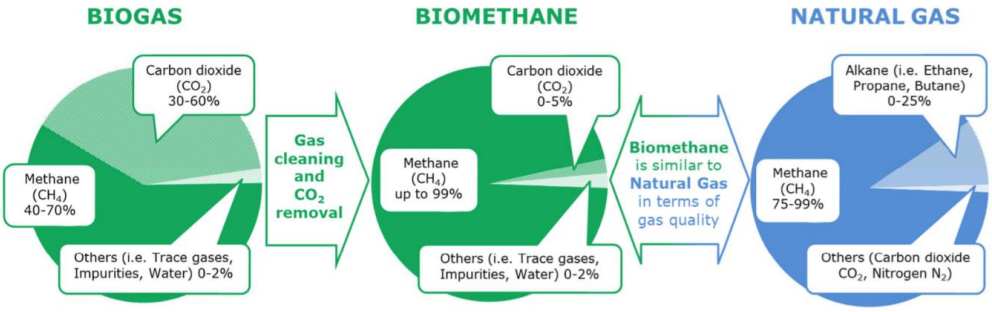

Figure 1. Biogas upgrading to biomethane process [3].

In this work, two metal-zeolites containing Ni or Ru and a commercial Ni-based catalyst were studied under biogas upgrading conditions. Catalysts were characterized, before and after reactivity tests, by XRD, H_2-TPR, N_2 adsorption and TGA, and tests were performed in a laboratory scale catalytic unit using a feed containing $CO_2/H_2/N_2$ or $CO_2/H_2/CH_4$ mixtures (P_{CO2}=0.16 bar and P_{H2}=0.64 bar in both cases).

The active metal nature significantly influenced the reducibility properties and the metallic dispersion, being well-dispersed Ru species reducible below 200 ºC formed in the Ru/Zeolite catalyst. In terms of catalytic performances, no remarkable effects were derived by the incorporation of CH_4 in the feed, evidencing the suitability of zeolite-supported catalysts for this application.

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P81

Development of MgO-based sorbents for CO_2 capture at medium temperature

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The energy demand and the industrial development led to a continuous increase of CO_2 in the atmosphere. To minimize this problem, carbon capture and storage/utilization technologies emerged during the last decade. Post-combustion adsorption technologies allow the separation of CO_2 from the flue gases and the main challenge is the selection of a proper sorbent: high and stable adsorption capacity, fast adsorption and desorption kinetics and adequate mechanical strength. At intermediate-temperature range (200-400 ºC) the MgO-based materials have recently attracted considerable research interest, owing to their low price, high theoretical CO_2 capture capacity (1.09 g CO_2 /g MgO) and low regeneration energy which allows reducing the energy consumption impact on system efficiency.

The main drawback of using MgO sorbents for CO_2 capture is its poor sorption capacity coupled with slow kinetics. Therefore, several techniques like the dispersion of MgO on porous inert supports, the use of different precursors or the doping with alkali salts, have been proposed to improve the CO_2 capture performance of MgO-based sorbents. A promising methodology is the doping with alkali metals salts (AMS), since the AMS act as CO_2 capture promoters by providing an alternative pathway which occurs at the sorbent-gas interface typically called as triple phase boundary.

In this work, a MgO-based sorbent was successfully synthesized by the sol-gel technique, using the $Mg(NO_3)_2.6H_2O$ as sorbent precursor and citric acid (Figure 1.a). Based on the thermogravimetric (TG) decomposition profile, the wet sol-gel was calcined at 500 ºC and MgO crystallites with ca. 10 nm were identified by X-ray diffraction (XRD) technique (Scherrer equation). To enhance the sorbent CO_2 capture capacity, the MgO was dopped with AMS and characterized by XRD (Figure 1.b). The AMS doping allows increasing the sorbent CO_2 carrying capacity, and 0.5 g CO_2/g sorbent (300ºC, 60 min, 100%CO_2) was captured in a TG experiment.

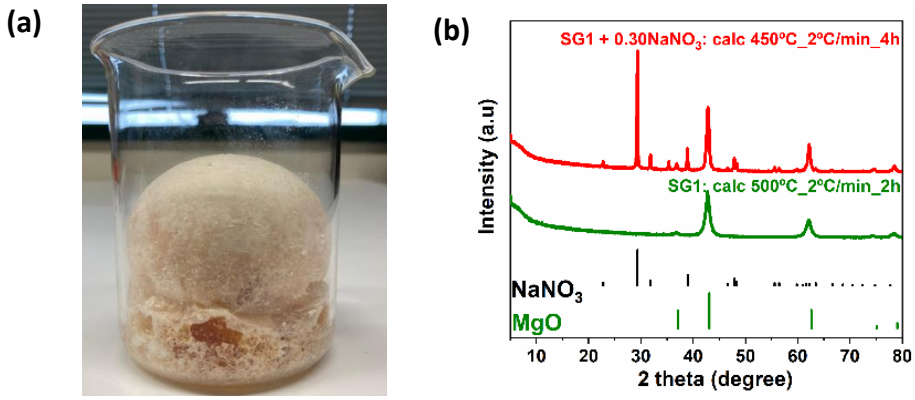

Figure 1. MgO based sorbents: (a) wet sol-gel, (b) XRD pattern of calcined sol-gel before and after AMS doping.

Acknowledgements
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P82

Reactivity of dithiolate gold(I) complexes with molecular O_2 in the gas-phase

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We have previously prepared a gold(I) cationic complex, $[Au(CH_3CN)_2]^+$, from a gold(III) salt, in the gas-phase, that is very reactive with different light, inert and noble gases, forming $[Au(CH_3CN)_2(L)]^+$ complexes with L= Xe, N_2, N_2O, NO, CO, COS, CS_2, CH_4, C_2H_6, C_2H_4, but no reactivity with molecular O_2 was observed [1]. Following these previous results, we decided to test the reactivity of other gold(III) salts prepared in the condensed phase, namely the gold(III) dithiolate salts TPP[Au(qdt)$_2$] (qdt = quinoxaline-2,3-dithiolate) and TBA[Au(mnt)$_2$] (mnt = 1,1-dicyanoethylene-2,2'·dithiolate) [2].

We used electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT-MS) to produce the $[Au(qdt)_2]^-$ and $[Au(mnt)_2]^-$ complexes from TPP[Au(qdt)$_2$] and TBA[Au(mnt)$_2$] solutions in CH_3CN, respectively, directly injected into the ESI source. CID (collision-induced dissociation) of $[Au(qdt)_2]^-$ and $[Au(mnt)_2]^-$ showed the formation of $[Au(qdt)]^-$ and $[Au(mnt)]^-$, respectively, that reacted promptly with O_2 present in the ion trap background, instigating an Au - O_2 interaction. As demonstrated on Fig. 1, the $[Au(qdt)]^-$ anionic complex is much more reactive than the $[Au(mnt)]^-$ complex; minor reaction with N_2, from the ion trap background, was also observed. These experimental studies are being complemented with computational calculations to assist the interpretation of the reactivity of the $[Au(qdt)]^-$ and $[Au(mnt)]^-$ complexes.

The well-known low affinity for gold binding to oxygen [3] give rise to compounds that are rather unstable but, on the other hand, weak bonds are usually highly reactive so these gold compounds containing Au-O bonds are expected to display an interesting reaction chemistry with relevance for organic synthesis and catalysis areas.

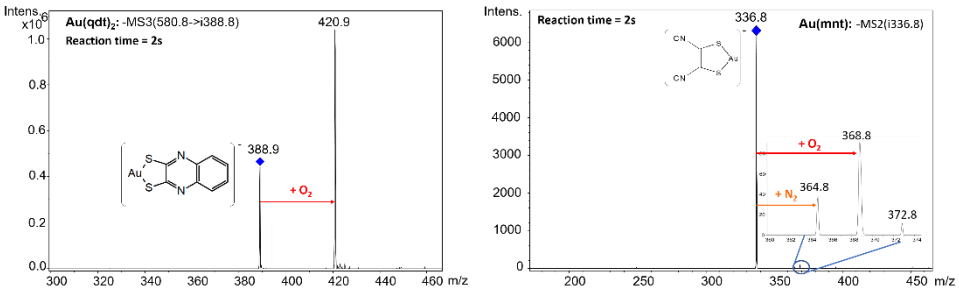

Figure 1. Mass spectra showing coordination of O_2 to $[Au(qdt)]^-$ (left) and $[Au(mnt)]^-$ (right) at 2 s reaction time.

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P83

On route to new ruthenium-based olefin metathesis catalysts with *cis* stereochemistry

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Ruthenium-based complexes with *cis* stereochemistry are an interesting and mainly unexplored class of olefin metathesis catalysts. This geometry is achieved by chelating ligands. We report here the synthesis of pyridine functionalized phosphines obtained by a simple two-step procedure.[1] Two different approaches were attempted to introduce the ligand: i) Reactions of the ligands with $[Ru(cod)_xCl_2]$[2] in the presence of hydrogen, that gave different results depending on the ligand. Di-tert-butylpyridylphosphine led to an unexpected break of a C-P bound and the formation of a P-H bond, **2.1**, while 2-((di-tert-butylphosphanyl)methyl)pyridine led to **2.2**; ii) Reaction with $[Ru(PPh_3)_3Cl_2]$ allowed the introduction of the ligand, giving the expected complex **3** as well.[3] Attempts to introduce the alkylidene ligand are currently underway. Single-crystal molecular structures of one ligand and all the complexes obtained are presented.

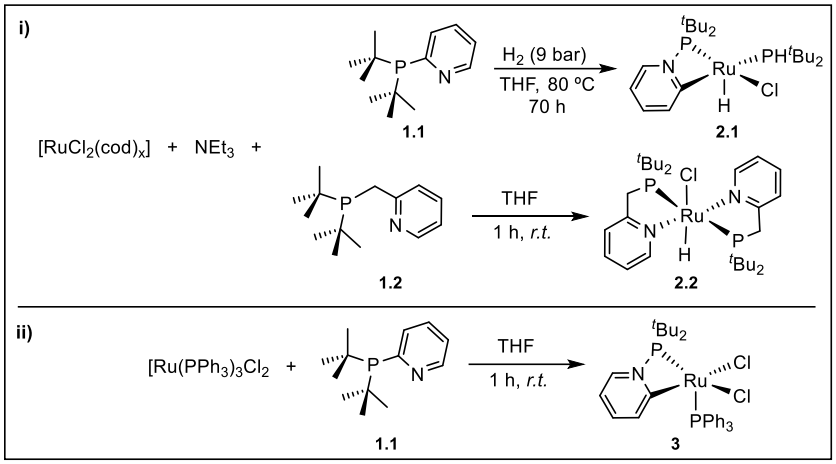

Figure 1. Synthesis of new ruthenium complexes.

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P84

Reductive depolymerization of plastic waste catalyzed by $Zn(OAc)_2.2H_2O$

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Plastics make our lives much more convenient. As a consequence, the enormous plastic consumption has led in parallel to the generation of plastic waste, which has become one of the biggest problems all over the world.

This communication reports the first methodology for the reductive depolymerization of plastic waste using a zinc catalyst. The commercially available, very cheap, and environmentally friendly compound $Zn(OAc)_2.2H_2O$ proved to be an efficient catalyst for the reductive depolymerization of polycaprolactone (PCL), polylactic acid (PLA), polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) waste using a silane as the reducing agent into value-added compounds including 1,6-hexanodiol, 1,2-propanediol, *p*-xylene and THF in good yields (Fig. 1).

This work demonstrates that it is possible to efficiently recycle plastic waste obtained from domestic waste or generated from different industries including textile or automobile, using a simple, eco-friendly, commercially available and inexpensive catalyst, contributing to reduce the large amount of plastic waste that is released into the environment and into the oceans and also to improve the circular economy and human health.

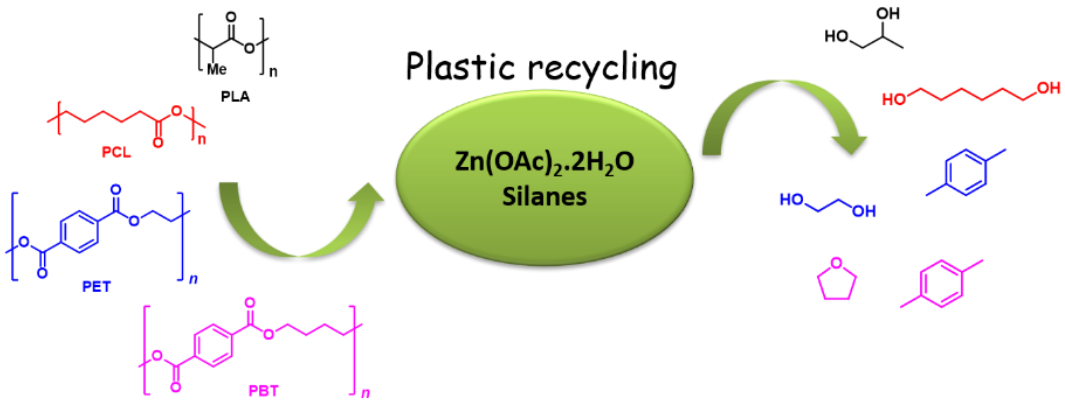

Figure 1. Plastic recycling with the catalytic system $Zn(OAc)_2.2H_2O$/Silane.

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P85

A sustainable protocol for the oxidation of 1-phenylethanol catalyzed by Fe@hierarchical zeolites

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The pursuit for innovative catalytic systems has encouraged the development of environmentally friendly processes and sustainable production of novel materials. Desilicated zeolites, that present additional porosity in the mesopore range obtained through a simple alkaline treatment using organic or inorganic bases [1], have been used as supports for the immobilization of metal and metal complexes, involving the immobilization of the metal salt in solution. Recent studies have reported the mechanochemical preparation of iron-immobilized species onto zeolites and their application in selective microwave-assisted oxidation reactions [2]. In this work we explored the additive-free oxidation of 1-phenylethanol to acetophenone by aqueous hydrogen peroxide using cheap and commercially available Fe chloride immobilized in hierarchical BEA zeolites by mechanochemical grinding (Figure 1). The most encouraging results were obtained for sample **Fe@BEA0.2AT,** with 35% yield and 56 % selectivity to acetophenone, allowing five reuse cycles without significant loss of activity and selectivity. This sustainable protocol allowed energy and time saving of the overall process, highlighting the advantages of mechanochemistry and the use of MW-irradiation.

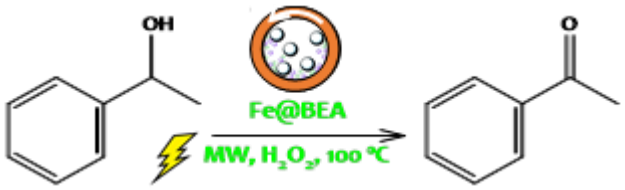

Figure 1. MW-assisted oxidation of 1-phenylethanol to acetophenone with hydrogen peroxide catalyzed Fe@BEA materials.

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P86

Novel cyclam derivatives for antimicrobial applications

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Multidrug-resistant human pathogens are a major concern for nowadays society being crucial the development of more efficient antimicrobials. Macrocyclic polyamines have generated a great interest over the last years because of their chemical and biological properties.[1] In particular, cyclams have found several applications in medicine as anticancer [2], antimalarial[3], and antischistosomal[4] agents. More recently, a new family of cyclam derivatives were screened for their antimicrobial properties.[5] The *trans*-disubstituted cyclam derivative of formula $H_2(^{4\text{-}CF3}PhCH_2)_2$Cyclam (see Figure 1a) was found to be highly active against both Gram-positive and Gram-negative bacteria.[6]

The work presented herein is based on applying Crystal Engineering principles for the design and synthesis of new co-crystals [7] with $H_2(^{4\text{-}CF3}PhCH_2)_2$Cyclam. Several antibiotics and other biologically active co-formers (ex: flufenamic acid, biotin, or acetylsalicylic acid) are being explored seeking for synergistic effects. Since pharmaceutical industry needs cleaner, safer, and more efficient transformations, mechanochemistry is the main synthetic technique that has been used in these studies.[8]

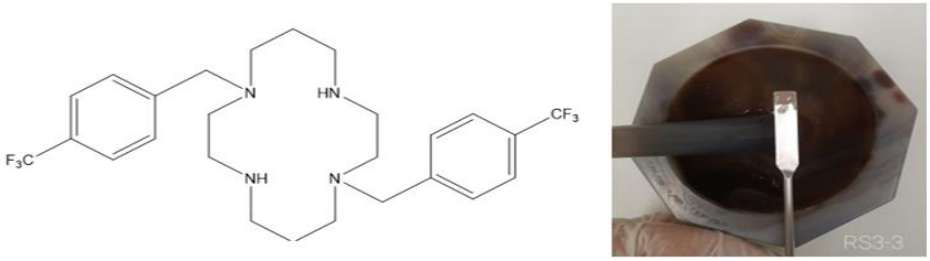

Figure 1. (a) Structure of $H_2(^{4\text{-}CF3}PhCH_2)_2$Cyclam (b) reaction product obtained by mechanochemistry.

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